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COMPOSITION DEPENDENT EFFECTS IN
GAS CHROMATOGRAPHY

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National Aeronautics and Space
Administration

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Analysis and Design of a Capsule Landing System
and Surface Vehicle Control System for
Mars Exploration

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ABSTRACT

Continuing research sponsored by NASA is concerned with developing fundamental concepts which are required to optimize a gas chromatograph - mass spectrometer chemical analysis system suitable for use on an unmanned roving vehicle for Mars exploration. Prior efforts have developed simulation models for the chromatograph which have been compared with data obtained from a test facility. Representation of binary systems by superposition was previously shown to be a first-order approximation and in certain cases large discrepancies were noted. This subtask had as its objective the generation of additional binary data and analysis of the observed nonlinear effects.

Modifications were completed on the test facility and data analysis programs to improve accuracy of the results. Data were gathered on the porous C-102 column and the nonporous C-1500 column for pentane, heptane, acetone, methyl ethyl ketone, and ethylene at various temperatures and system conditions.

The thermodynamic parameter mR_o for heptane on C-102 was found to vary linearly with component concentration in the gas. This paralleled the nonlinearity observed in the pentane-heptane binary system on C-102. Simulation was improved as the system composition became more dilute. A similar effect was observed for ethylene on C-102. Experiments with the pentane-heptane on a DES column showed the system to be well modeled by the equilibrium

adsorption model and superposition. This demonstrated that the extent of the composition dependent effect was specific to each chemical-adsorbent system.

The theoretical Langmuir isotherm was examined as a possible means to account for this composition dependent effect. Orthogonal collocation was used to solve the equilibrium adsorption model using the Langmuir isotherm instead of the linear isotherm. The resulting solutions show qualitatively that the isotherm models actual column behavior. Quantitatively, simulation was inadequate and further experimentation with the numerical solution of this nonlinear partial differential equation is required.

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I. INTRODUCTION

This report describes recent work done on multicomponent gas chromatography as part of an effort to design chemical analysis equipment for the unmanned martian roving vehicle being developed at Rensselaer. The overall task is to provide design criteria and engineering techniques to build an optimum system. The plan is to couple a gas chromatograph used to separate mixtures, with a mass spectrometer capable of analyzing chemical components. This system must be flexible enough to perform a variety of tasks including atmosphere analysis, pyrolytic tests, and incubation tests of soil and atmosphere samples to detect possible biological activity on mars. The most crucial design specification for this system is that it be small enough and light enough to fit on board the vehicle.

Gas chromatography is a means of separating a mixture of differing chemical species by utilizing the dynamic mechanism of adsorption - desorption between a packed bed and a flowing inert gas stream. Separation occurs because of differences in the adsorption isotherms of the various components. The more strongly a component is adsorbed the longer its elution time will be. In an ideal system an input pulse containing a mixture of components will elute as a series of pulses each containing one of the components.

A gas chromatograph can be used for much more than separating mixtures however. A composition detector at the outlet of the column can monitor the area of each component pulse. This area is related to the percentage of that component in the original sample. The relative amounts of the components can be calculated and a good guess at the identification of each species can be made, since each substance elutes from a given column at a characteristic time. The mass spectrometer provides positive identification.

Since gas chromatography is a complex process with many dynamic mechanisms continually taking place, mathematical models are being developed to predict system behavior under a wide variety of conditions. These predictions are compared to actual data. Deviations from experimental results point out the flaws in the models. Theoretically an exact model which would incorporate all phenomena observed in chromatography could be developed. However, the complexity of such a model would make its numerical solution impractical even with present day computers.

One must be satisfied with models describing only the most significant phenomena affecting the behavior of the column. These simple models can approximate reality to the extent that they are based on valid assumptions. If an important mechanism is not included in the model, predicted results will deviate from experimental results in a consistent and recognizable way. The model must then be amended. In this way, the actual conditions are identified where each physical phenomenon is

significant to the overall process. Simplified but valid models are the result.

Special problems arise in the study of multicomponent chromatography. The possibility of interaction between the various components, and other nonlinearities must be considered. The first approach to this problem is to assume no interaction between the components and to use linear superposition of individually modeled responses to predict the overall response. In fact when this approach was tried large deviations from experimental data were found for one column, the Chromosorb 102. The work presented here clarifies the cause of the deviations and explores the use of a model incorporating the nonlinear Langmuir isotherm to explain them.

II. SUMMARY

The gas chromatograph facility has been modified to improve the usefulness and accuracy of the data. A sleeve added to the liquid injection block has caused syringe injected input pulses to the column to be narrower than had been attained previously. A change in the circuitry of the detector controllers has made possible continuous attenuation of the output signal to the recorder.

The computer programs used to analyze data have been updated to provide more information. The General Data Reduction Program was modified to report compositions as actual mole fractions and a moment analysis has been performed on the input and output pulses for comparison with moments predicted from models. A program for modeling binary systems, using linear superposition has been written and can be used to predict the separation of two components for any set of conditions.

New data have been gathered on the porous Chromosorb 102 column and the nonporous Carbowax 1500. Binary samples could not be separated on the C-1500 column. Experiments on a new nonporous column with a coating of di-2-ethylhexyl sebacate (DES) have shown that its behavior is extremely well modeled by the equilibrium adsorption model. Pentane-heptane mixtures can be separated on this column and linear superposition of pure component data models this behavior quite well.

Experiments using various volumes of heptane on the Chromo-sorb 102 column have shown that the parameter mR_0 for this system is a function of the amount of component present in the inert gas stream and is not strongly affected by the presence of other components. The nonlinear Langmuir isotherm has been proposed for the model to account for this effect.

This new model is nonlinear and cannot be solved analytically. The method of orthogonal collocation as developed by Woodrow was adapted to this problem. Results indicate that the method in its present form is not suitable for quantitative analysis of the model. On a qualitative basis the solutions obtained indicate that a nonlinear isotherm of the Langmuir type can predict the deviations from simpler models, observed on the C-102 column.

III. BACKGROUND

A substantial amount of experimental work has been completed on the chromatograph test facility, over a wide range of temperatures, pressures, flow rates and input pulses, using several columns and chemicals with different physical and chemical characteristics. In this way a variety of situations has been studied where different physical phenomena gain or lose influence on chromatograph behavior. So many phenomena are possible that only a complete model would be able to predict the observed results in every situation.

Previous investigators have contributed to the development of mathematical models to predict the behavior of gas chromatograph systems (Keba and Woodrow, 1972; Neisch, 1973; Sliva, 1968; Taylor, 1970; Voytus, 1969). The most useful of these models has been the equilibrium adsorption model which successfully predicts first order and in some cases second order behavior. This model takes into consideration axial interparticle diffusion, convection and equilibrium adsorption-desorption using a linear isotherm. The derivation of this model has been shown by Voytus(1969). In its mathematical form, the model is represented by the following partial differential equation which is a mass balance for the injected species in the fluid and solid phases of the column.

$$(1 + 1/mK_o) \partial y / \partial \theta = (1/Pe) \partial^2 y / \partial z^2 - \partial y / \partial z$$

Boundary Conditions:

$$y(0,0) = \text{input pulse}$$

$$\lim_{z \rightarrow \infty} y(z,0) = \text{finite}$$

The final solution of this equation is the following convolution integral:

$$y(z,0) = \int_0^{\theta} y(0, \theta - \tau) \cdot y_f(\tau) d\tau$$

where:

$$y(0,0) = \text{the input pulse}$$

$$y_f(\tau) = \text{the unit impulse response at the end of the column}$$

$$= 1/2 \sqrt{\frac{\beta Pe}{1 + \tau^2}} \exp \left\{ -\frac{Pe}{4\beta\tau} (\tau - \beta)^2 \right\}$$

where:

$$\beta = (1 + 1/mR_0)$$

The Peclet number is a measure of the dispersion of the sample component due to axial diffusion in the column. Smaller values of Pe indicate greater dispersion. The thermodynamic parameter mR_0 determines the elution time of the injected component. Larger values of mR_0 indicate that a component is not strongly adsorbed in the column and that it will elute at a sooner time. This model does not consider intraparticle phenomena, adsorption-desorption kinetics or nonlinear isotherms. The importance of intraparticle phenomena is not yet well known. A study of the nonequilibrium adsorption model has shown that mass transport between the carrier gas and the adsorbent is too fast to have any limiting effects on systems studied thus far. The question of nonlinear isotherms is discussed in this paper.

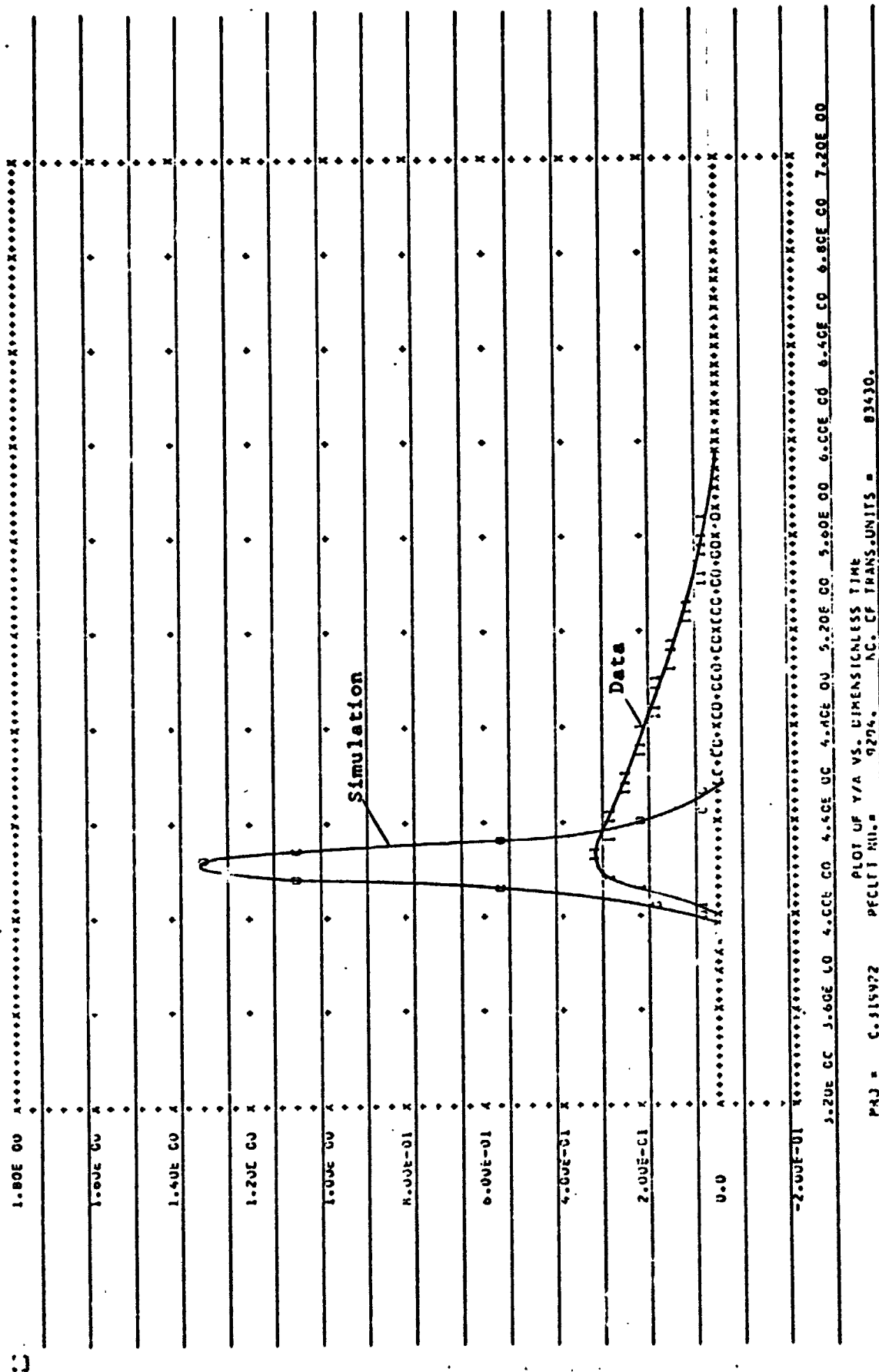
The equilibrium adsorption model was solved using numerical convolution with the computations being performed with the General Data Reduction Program (GDRP). In the output of this program, model predictions are compared directly to actual data. In some situations, the model simulations predicted system behavior quite well, indicating that all major dynamic phenomena had been accounted for. In a few situations the model predictions deviated consistently from actual data.

The most notable deviation occurred with ethylene on chromosorb 102. Figure 1 compares the model to actual data and there is little resemblance between the two. The actual output is very spread with much tailing, while the modeled response is a relatively sharp peak. When heptane was used on the C-102 column there was also more spreading in the actual data than in the simulation.

Another type of deviation was found when a binary mixture of pentane and heptane was used as the sample input on the C-102 column. The two species were separated but Meisch (1973) found that the parameter mR_0 was a significant function of composition. Figure 2 shows how the composition dependent mR_0 shifted the peaks of the actual data away from the model which is based on the linear superposition of pure component simulations. The figure also shows extra spreading of actual data that is not predicted by the model.

The equilibrium adsorption model obviously does not represent all of the physical behavior that is occurring in the column.

PLOT OF SIMULATED AND ACTUAL SYSTEM RESPONSE, U= SIMULATED OUTPUT, 1= ACTUAL SYSTEM DATA



ETHYLENE ON A CHROMASORB 102 COLUMN, 75 DEG. C, 43 CC/MIN. HELIUM
NOV-ELUTIONION AUG-PTIC, ACHIL

Figure 1 Simulated and Actual Chromatographic Data for Ethylene on C-102 at 75° C.

Figure 2 Simulated and Actual Binary Data for Pentane And Heptane on C-102

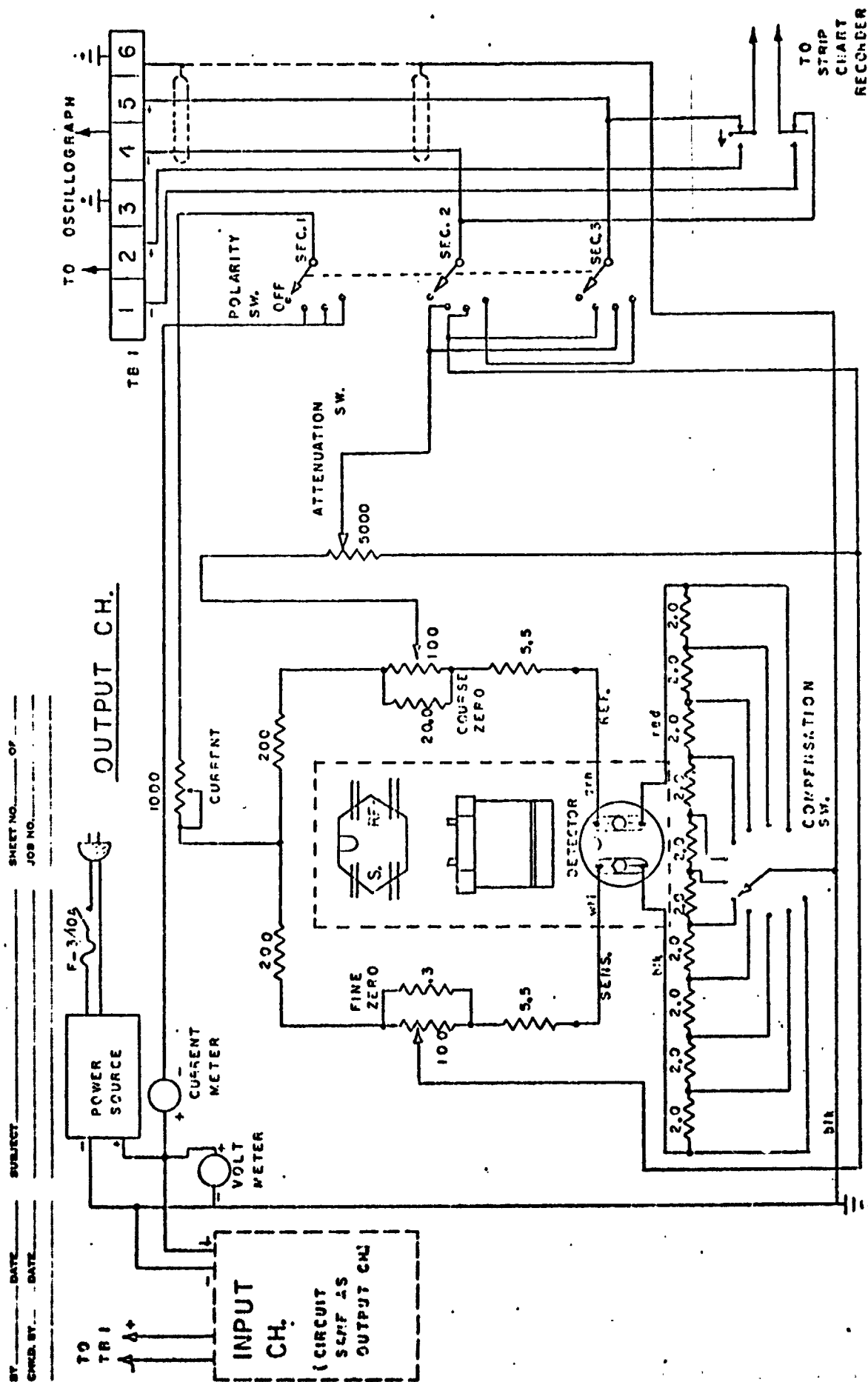
There are many possibilities to consider. Meisch's findings concerning the porosity of the column packing, support the notion that intraparticle diffusion is present. Woodrow (1974) is working on this question. The variation of m_{Ro} with composition supports the idea that a nonlinear isotherm should be used in the model. This idea is investigated in this paper. Perhaps both situations are involved. The question is difficult to resolve because of problems encountered in solving the resulting mathematical models.

IV. RESULTS AND DISCUSSION

A. Modification of Equipment

All experimental gas chromatograph work has been done on a test facility which was described by Baer and Benoit (1971). Though this equipment had been proven adequate it needed improvement to increase the accuracy of the data it provided. Meisch (1973) pointed out that the ten position attenuator on the detector control was not a versatile enough adjustment to give full scale readings on the oscillograph recorder for the range of samples studied. This limitation decreased the relative accuracy of the data. In most cases a setting of one caused the readings to go off scale while the next setting of two caused deflections less than half the width of the strip chart. The ten position attenuator was replaced with a potentiometer, making continuous attenuation possible. The new circuitry is shown in Figure 3.

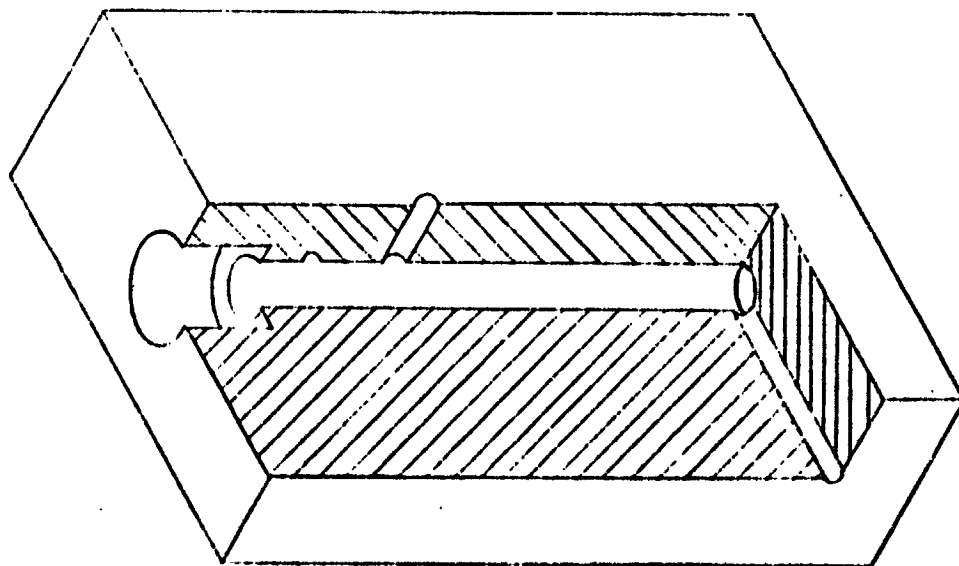
In separating a mixture of components on a gas chromatograph, it is desirable to use as narrow an input pulse as possible. This fact can be illustrated using moment analysis. It has been shown that the variance, or second moment about the mean, of the eluted peak is equal to the sum of the variances of the input pulse and the impulse response predicted by the model (Voytus, 1969). The width of a pulse is related to the square root of the variance. In order to ensure that a sample will be separated, the variance of the eluting peaks should be small to prevent overlapping.



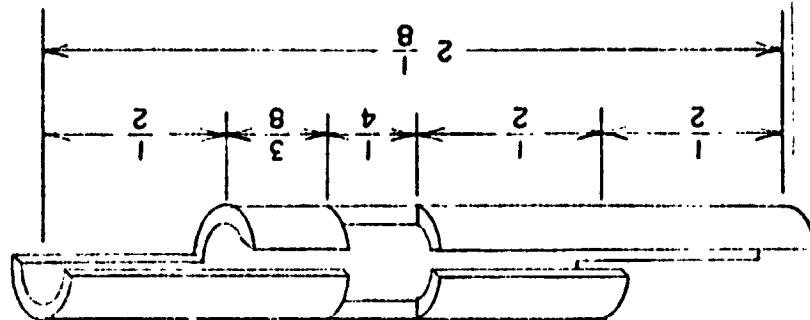
CARLE DETECTOR CONTROL CIRCUIT — FIG. 3

A study of the liquid injection system showed that the peak of the input pulse occurred as much as 15 seconds after the actual syringe injection. The cause of this spreading was found to be an excessively large vaporization chamber in the injection block. As shown in Figure 4, the injection chamber is formed by a cylindrical hole drilled from the top of the block to within a half inch of the bottom. A cylindrical heater is placed in the chamber, sealing the top of the block. It is immersed in the stream of helium which enters at the top of the block and leaves at the bottom. The sample is injected through a septum which is located near the entrance of the inert stream. In order to reduce the dead volume a tubular sleeve was designed which fills most of the space between the heater and the chamber wall. As is shown in Figure 4, the sleeve has slots which channel the gas stream directly through the chamber. To be sure that the liquid sample would completely vaporize in the smaller residence time, the wiring was changed to give continuous full power to the block heater.

Figure 5 shows how the addition of the tubular sleeve to the injection chamber has narrowed the input pulse. Under the same flow conditions with two equal sample sizes, the peak of the input peak occurs at 10 seconds before the change and at 3 seconds after the change. There is also a substantial decrease in the variance which was 131. before and 25. after the sleeve was added. It should be noted that the characteristics of the input depend on many factors including flow rate, sample size



INJECTION BLOCK

VOLUME REDUCTION
INSERT

O.D. = .2500
I.D. = .1960

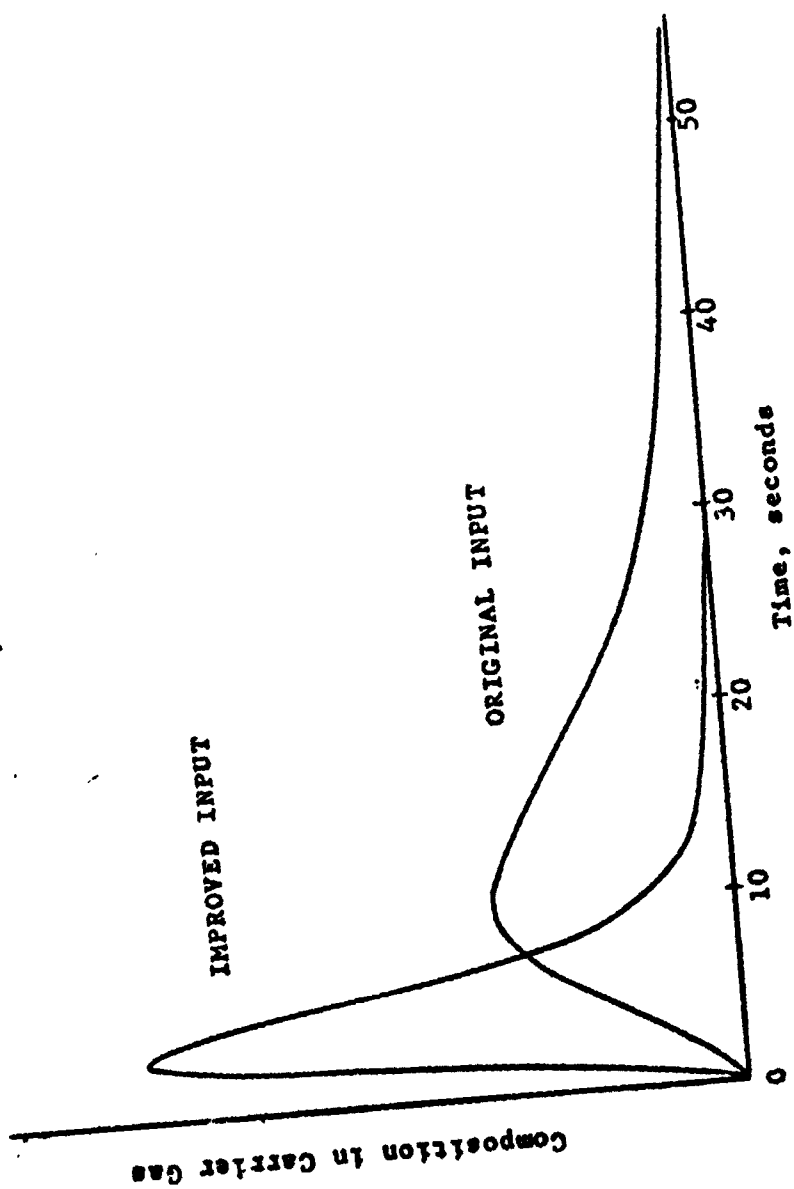


Figure 5 Input Pulse to Column for Liquid Samples

amount of time taken to depress the syringe, positioning of the syringe and condition of the rubber septum. It has been found for example that narrower input pulses result when new septa are used.

B. Linearity of the thermistor probe

While the accuracy of the data gathered on the gas chromatograph facility depends on the equipment, the validity of these data depends on correct interpretation of the information received. Data processing methods assumed linearity between the electrical signal produced by the thermistor probes of the detectors and the composition of the sample in the carrier gas. A simple experiment was devised to verify this assumption.

The column was operated at constant flow rate and temperature. The electrical controls were set so that a $3.0 \mu\text{l}$. sample of heptane would register a full scale deflection on the oscillograph recorder. This input pulse was recorded and subsequently a $1.5 \mu\text{l}$. sample was injected and its pulse was recorded. A similar procedure was followed for a $2.0 \mu\text{l}$. and $1.0 \mu\text{l}$. sample. Linearity of the detection system would cause the area under the curves to be proportional to the sample size. The areas were computed and the results follow in Table I.

TABLE I

Data Concerning the Output of the Thermistor Probe

	<u>Sample 1</u>	<u>Sample 2</u>	<u>Ratio of Areas</u>
Test 1	$3.0 \mu\text{l}$	$1.5 \mu\text{l}$	1.948
Test 2	$2.0 \mu\text{l}$	$1.0 \mu\text{l}$	2.073

The ratio of areas should be 2.0 in both cases if the sample sizes are accurate and the detector is linear. The actual results are about 3.0% low in the first run and 3.5% high in the second. Considering the limited accuracy in experimental technique and in computations of the areas, the deviations are not significant. The thermistor detector appears to be linear in the composition range of interest.

C. Modification of Data Processing

Some of the computer programs used for data analysis have been changed and new programs have been written to increase the amount of information they provide. The General Data Reduction Program has been modified to read in the sample size of the input pulse and the flow rate of the carrier gas so that it now reports input and output compositions as actual mole fractions rather than as normalized concentrations. This information is useful in comparing compositions of input pulses of different sizes and shapes. It also can provide information concerning the concentrations of sample in the carrier gas at which composition dependent nonlinearities might be significant. Subroutine STATMO, written by P. Woodrow (Appendix A), was added to the program. It calculates the first moment about the origin and the second and third moments about the mean for the input and output pulses, and reports them in both dimensionless and real time domains. These moments are useful when the moments of a model can be calculated from the Laplace transform of the model. By comparing the moments of the model to the actual moments,

a model can be quickly verified without obtaining a time domain solution. This technique has proved feasible for a complicated inter-intraparticle model (Woodrow, 1973).

The method of analyzing binary data has been revised somewhat. Figure 6 is a schematic of the new procedure. The Binary Analysis Program, written by P. Keba (1972), requires the input of simulated and actual data points. This program itself has been changed only so that it reports compositions as actual mole fractions. A new program, SIM has been written which uses the input pulse and system parameters of the binary mixture and the mRc of the pure components at the same temperature to simulate the system and punch the simulated chromatogram data points on data cards. The linear superposition of the pure component simulations is compared with the actual data by the Binary Analysis Program.

A program has been written for simulating the separation of a binary sample using information from pure component data. Figure 7 shows the organization of the program. System parameters such as column and packing dimensions as well as flow rates and types of input pulses can be varied to find the effect of each parameter on the output. This program has found several uses. It can predict if a column can be used to separate a given mixture with the limitations imposed by the experimental equipment. This information has guided the recent purchase of a new column. A revised version of this program has been used by Slovall (1974) to study resolution of partially separated peaks.

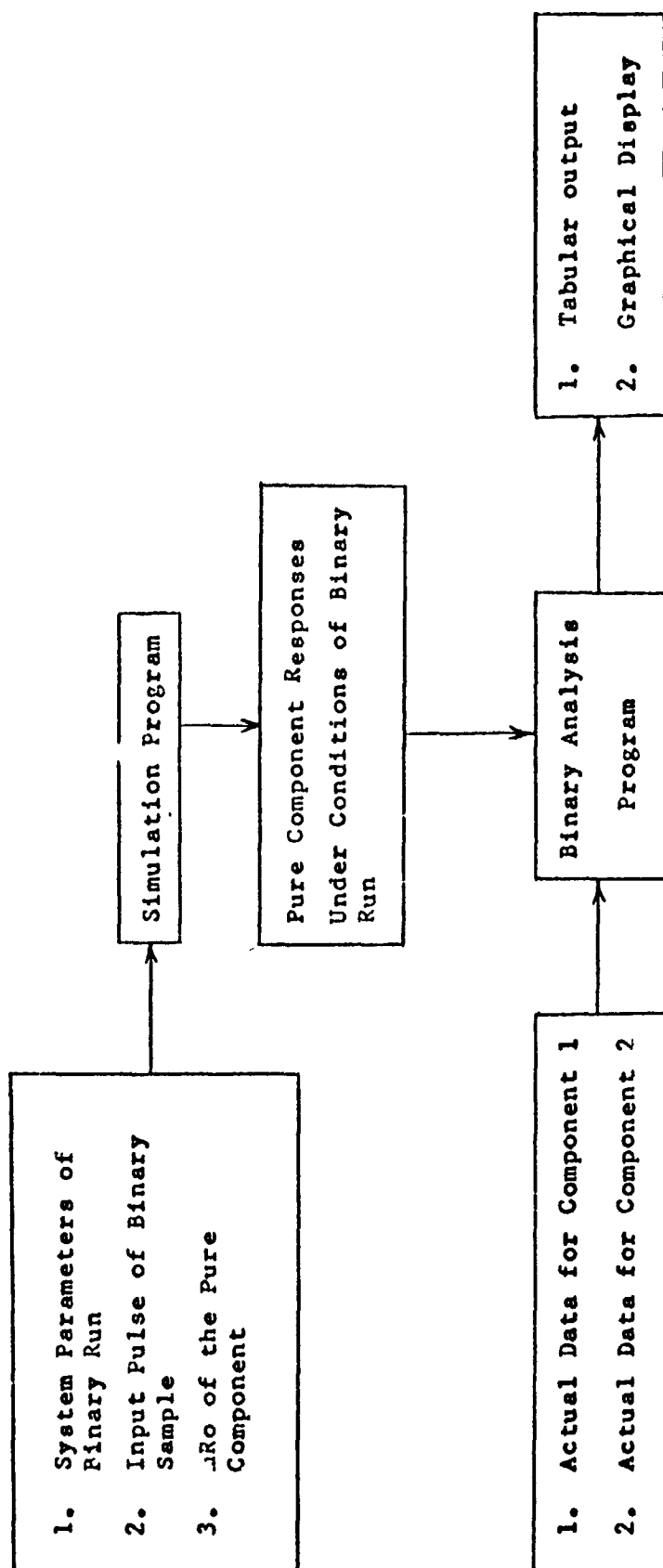


Figure 6 Procedure For Analysis of Binary Data

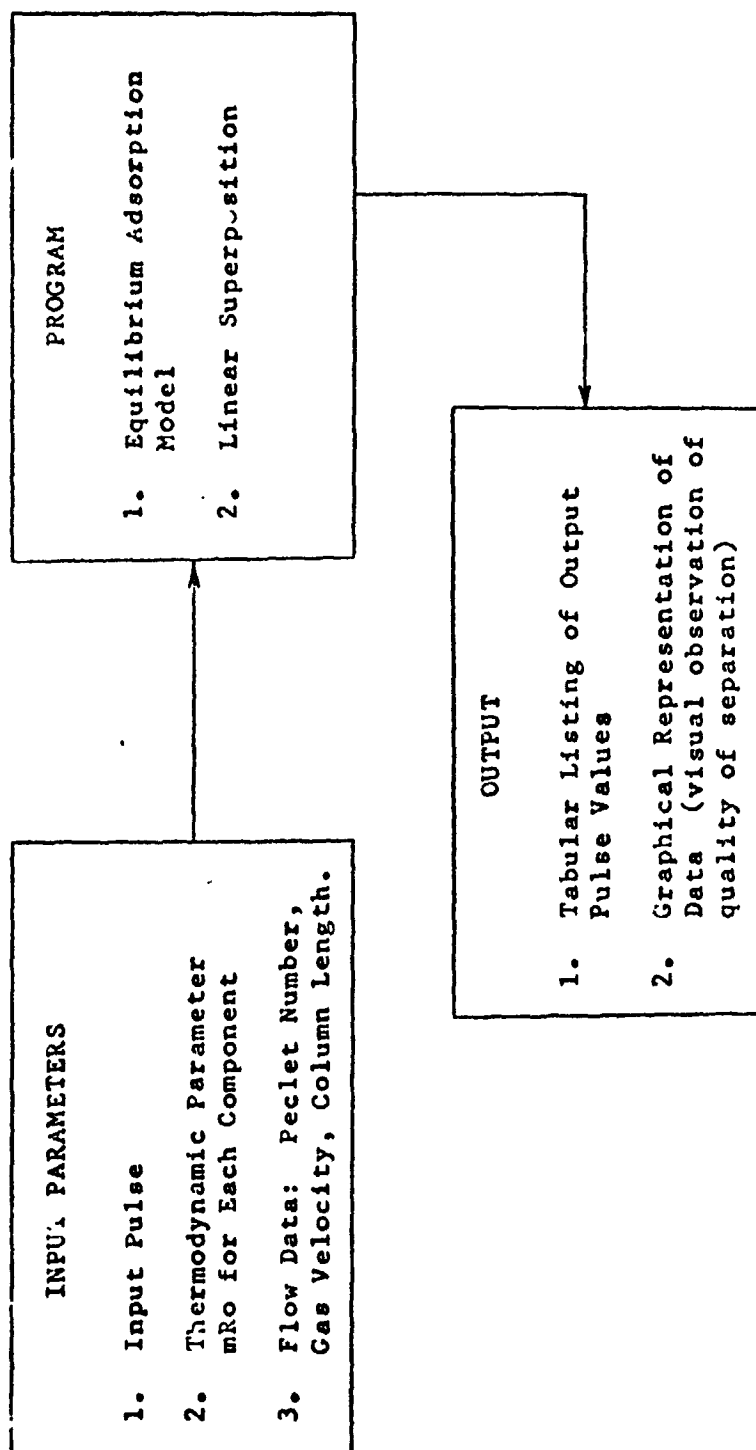


Figure 7 Binary Simulation Program MODEL

D. Summary of Data

For convenience, all of the chromatographic data obtained to the present has been summarized in tabular form. The system parameters, temperature, flow rate, gas velocity, Peclet number, N_{tog} and mR_o are reported for each run. In addition, the sample size and the time at which the input pulse reached a peak have been reported where possible to give a measure of the relative characteristics of different inputs.

Table II shows data for pentane, heptane, ethylene, methyl ethyl ketone and acetone on chromosorb 102. New data on this column include heptane at various sample sizes and methylethyl ketone. Table III reports binary data obtained on C-102. Figure 8 illustrates the variation of mR_o with temperature for mek on this column.

Data for the carbowax 1500 column are summarized in Table IV. New data include acetone and mek run over a range of temperatures, and ethylene at many temperatures, flow rates, sample sizes and with syringe injection. The variation of mR_o with temperature for pentane, heptane ethylene, mek and acetone are shown in Figures 9 through 13.

The new DES column has been tested with pentane and heptane. Pure component data are given in Table V, and binary data are in Table VI. The effects of temperature on mR_o for pentane and heptane are shown in Figures 14 and 15. The effects of sample composition in a binary mixture, and sample size on mR_o are shown in Figures 16 and 17. Dimensionless moments for

TABLE II

PURE COMPONENT DATA
ON CHROMOSORB 102

PENTANE (150°, 175°, 200°)

Temp °C	Sample Size μl	Input Peak sec	Flow Rate cc/min	Gas Velocity cm/sec	Peclet No.	N _{tog}	mRo
150°	2.0	12.5	29.4	21.13	9128	82640	0.0753
175°	2.0	12.0	30.0	22.84	8978	83960	0.1017
200°	2.0	12.0	26.4	21.22	7735	96560	0.1494

HEPTANE (150°, 175°, 200°)

Temp °C	Sample Size μl	Input Peak sec	Flow Rate cc/min	Gas Velocity cm/sec	Peclet No.	N _{tog}	mRo
150°	2.0	11.0	29.4	21.13	10690	70200	0.0177
150°	2.0	9.0	41.6	25.00	13770	53690	0.0184
175°	2.0	8.0	36.6	23.30	12140	61640	0.0383
175°	2.0	12.0	30.0	22.84	10520	71340	0.0320
200°	2.0	15.0	20.4	16.40	7211	102100	0.0711
200°	2.0	11.0	34.0	22.85	11100	67570	0.0698

TABLE II (cont.)

HEPTANE 200° C Varying Sample Concentration

Temp °C	Sample Size μl	Input Peak sec	Flow Rate cc/min	Gas Velocity cm/sec	Peclet No.	N _{tog}	mRo
200°	0.2	3.0	28.6	22.99	9781	76600	0.0482
200°	0.5	4.0	28.6	22.99	9781	76600	0.0514
200°	1.0	3.0	28.6	22.99	9781	76600	0.0547
200°	1.5	3.0	28.6	22.99	9781	76600	0.0590
200°	2.0	4.0	28.6	22.99	9781	76600	0.0611
200°	3.0	4.0	28.6	22.99	9781	76600	0.0666

ETHYLENE (20°, 28°, 50°, 75°, 100°, 125°, 150°, 175°)

Temp °C	Sample Size μl	Flow Rate cc/min	Gas Velocity cm/sec	Peclet No.	N _{tog}	mRo
20°	100	43.0	23.56	9250	83780	0.1225
28°	100	43.0	25.65	10210	76270	0.1117
50°	100	43.0	26.46	9744	79750	0.1942
75°	100	43.0	27.79	9294	83430	0.3199
100°	100	43.0	27.26	8821	87650	0.4230
125°	100	43.0	27.74	8446	91270	0.4785
150°	100	43.0	28.33	8102	94870	0.6008
175°	100	43.0	28.76	7793	98340	0.5869

TABLE II (cont)

Methyl Ethyl Ketone (150°, 175°, 200°)

Temp °C	Sample Size μl	Input Peak sec	Flow Rate cc/min	Gas Velocity cm/sec	Peclet No.	N _{tog}	mRo
150°	0.5	1.0	40.4	26.46	10850	70240	0.0371
175°	0.5	.75	40.4	28.02	10500	72610	0.0565
200°	0.5	2.0	42.6	29.60	10580	72070	0.0906

Acetone (100°, 125°, 150°, 175°, 200°)

Temp °C	Sample Size μl	Input Peak sec	Flow Rate cc/min	Gas Velocity cm/sec	Peclet No.	N _{tog}	mRo
100°	2.0	12.0	43.0	27.26	8689	88960	0.0286
125°	2.0	1.75	24.0	19.84	4938	148700	0.0576
125°	2.0	12.0	43.0	27.74	8309	92760	0.0527
150°	2.0	12.0	43.0	28.33	7965	96480	0.0968
175°	2.0	12.0	43.0	28.76	7652	100100	0.1219
200°	2.0	12.0	43.0	29.32	7388	103400	0.1734

TABLE III

BINARY DATA ON CHROMOSORB 102Pentane - Heptane 150°C

	Flow Rate cc/min	Gas Velocity cm/sec	Peclet No.	N _{tog}
Pentane	29.4	21.13	9128	82640
Heptane	29.4	21.13	10690	70200

Wt Fraction Pentane	Wt Fraction Heptane	Input Peak	Pentane mRo	Heptane mRo
.99	.01	13.0	0.0747	0.0116
.75	.25	13.0	0.0725	0.0137
.50	.50	10.5	0.0673	0.0153
.25	.75	11.0	0.0663	0.0163
.01	.99	11.0	0.0599	0.0171

TABLE III (cont)

Pentane - Heptane 175° C

	Flow Rate cc/min	Gas Velocity cm/sec	Peclet No.	N _{tog}
Pentane	30.0	22.84	8978	83960
Heptane	30.0	22.84	10520	71340

Wt Fraction Pentane	Wt Fraction Heptane	Input Peak	Pentane mRo	Heptane mRo
.99	.01	11.0	0.1022	0.0243
.75	.25	12.0	0.0988	0.0261
.50	.50	15.0	0.0945	0.0275
.25	.75	11.5	0.0925	0.0277
.01	.99	11.5	0.0895	0.0295

Pentane - Heptane 200° C

	Flow Rate cc/min	Gas Velocity cm/sec	Peclet No.	N _{tog}
Pentane	26.4	21.22	7735	96560
Heptane	26.4	21.22	9118	81960

Wt Fraction Pentane	Wt Fraction Heptane	Input Peak	Pentane mRo	Heptane mRo
.50	.50	11.0	0.1471	0.0531
.25	.75	12.0	0.1472	0.0553
.01	.99	11.5	0.1398	0.0582

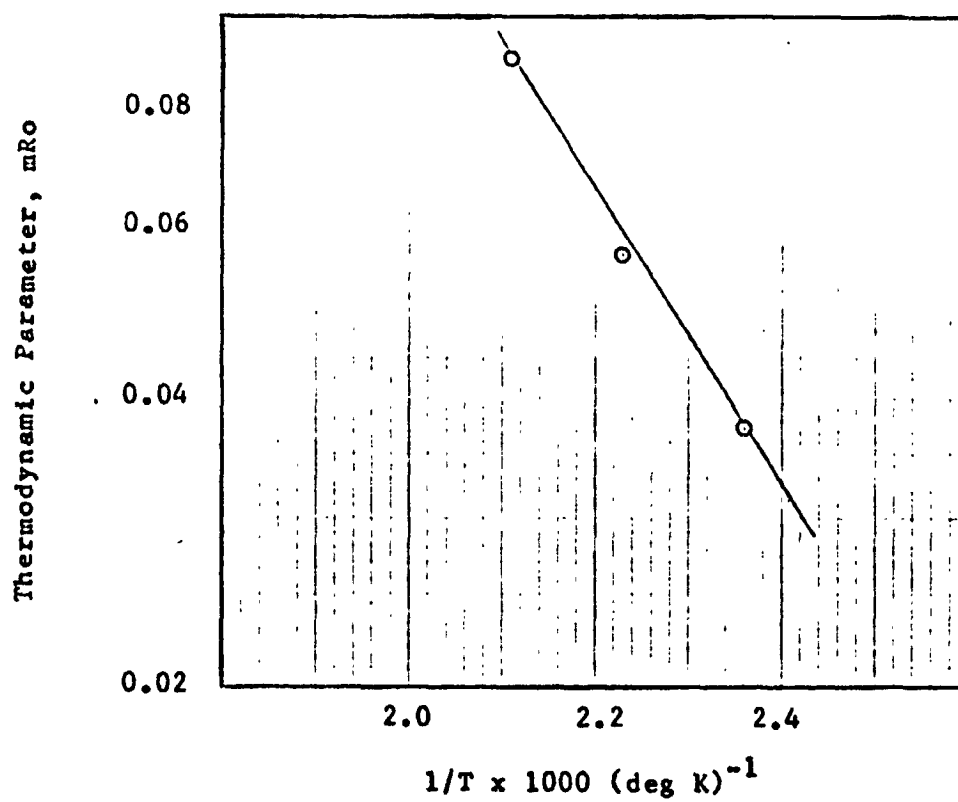


Figure 8 Effect of Temperature on Parameter mRo for Mek on Chromosorb 102

TABLE IV

PURE COMPONENT DATA
ON CARBOWAX 1500

ACETONE (75°, 100°, 125°, 150°)

Temp °C	Sample Size μl	Input Peak sec	Flow Rate cc/min	Gas Velocity cm/sec	Peclet No.	N _{tog}	mRo
75°	0.5	3.0	34.2	27.57	7654	100000	0.1315
100°	2.0	10.0	31.8	24.90	6757	112100	0.1875
125°	2.0	10.5	29.6	24.80	6051	123900	0.2342
150°	2.0	10.5	27.7	24.6	5457	136000	0.2632

PENTANE (75°, 100°, 125°, 150°)

Temp °C	Sample Size μl	Input Peak sec	Flow Rate cc/min	Gas Velocity cm/sec	Peclet No.	N _{tog}	mRo
75°	0.5	3.5	34.2	27.57	12020	62930	0.3333
100°	2.0	10.5	31.8	24.94	10780	70280	0.4566
125°	2.0	10.0	29.6	24.77	9763	77470	0.4280
150°	2.0	9.5	27.7	24.63	8878	84840	0.4541

TABLE IV (cont)

30

HEPTANE (75°, 100°, 125°, 150°)

Temp °C	Sample Size μl	Input Peak sec	Flow Rate cc/min	Gas Velocity cm/sec	Peclet No.	N _{tog}	mRo
75°	0.5	4.5	34.2	27.57	13810	53510	0.2440
100°	2.0	8.5	31.8	24.94	12500	59750	0.3315
125°	2.0	10.0	29.6	24.77	11390	65830	0.3846
150°	2.0	9.5	27.7	24.63	10410	72060	0.3711

MEK (75°, 100°, 125°, 150°)

Temp °C	Sample Size μl	Input Peak sec	Flow Rate cc/min	Gas Velocity cm/sec	Peclet No.	N _{tog}	mRo
75°	0.5	4.0	34.2	27.57	11060	68860	0.0915
100°	0.5	3.0	33.5	27.96	10400	73240	0.1520
125°	0.5	3.0	34.6	29.57	10240	74380	0.1947
150°	0.5	2.5	34.4	29.89	9772	77840	0.2439

ETHYLENE (50°, 75°, 100°, 125°, 150°, 175°, 200°)

Temp °C	Sample Size μl	Flow Rate cc/min	Gas Velocity cm/sec	Peclet No.	N _{tog}	mRo
50°	100	43.9	31.88	10110	76980	0.4247
75°	100	43.6	32.66	9571	81140	0.4135
100°	100	44.1	34.18	9239	83910	0.4157
125°	100	45.2	35.41	9026	85790	0.4167
150°	100	44.1	35.92	8488	90860	0.3950
175°	100	40.0	33.00	7455	102400	0.4683
200°	100	40.0	34.77	7207	105600	0.4288

TABLE IV
(cont)ETHYLENE 100° C. Varying Sample Concentration

Temp °C	Sample Size μmoles	Flow Rate cc/min	Gas Velocity cm/sec	Peclet No.	N _{tog}	mRo
100°	4.16	143.0	75.05	19100	34070	0.3184
100°	4.38	87.5	55.45	15400	49060	0.3278
100°	11.00	44.7	35.05	9363	82860	0.3669
100°	13.30	87.5	55.47	15400	49060	0.3297
100°	***	49.5	37.93	10200	76330	0.3160

*** Syringe injection of 500 μl.

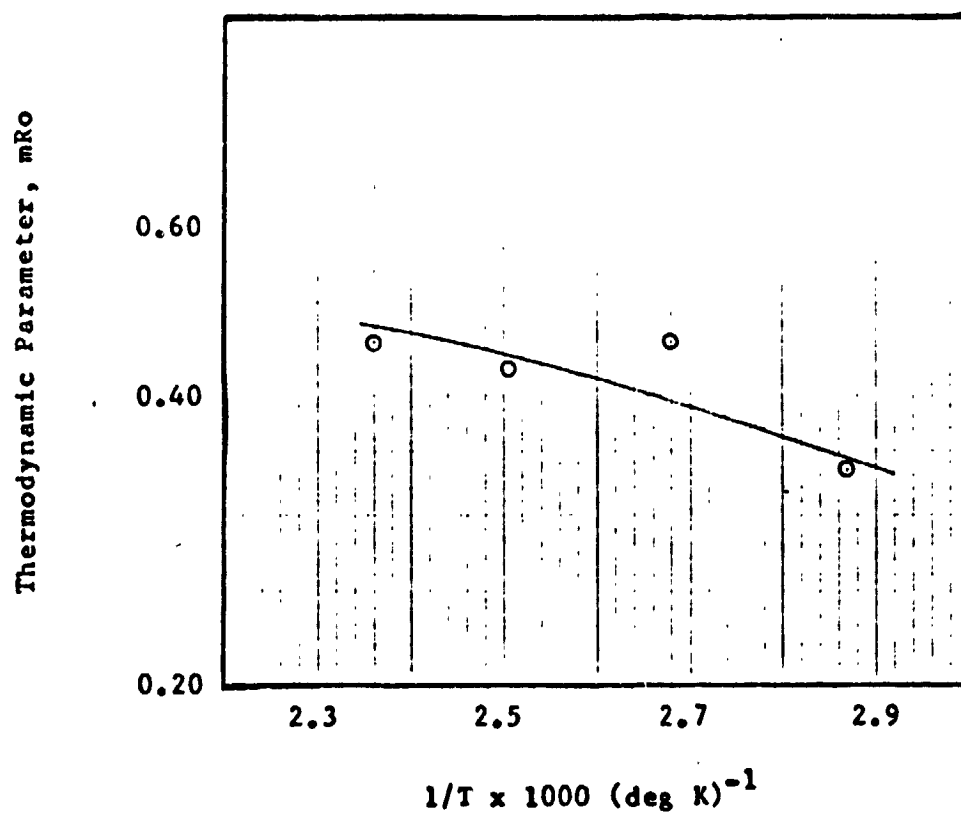


Figure 9 Effect of Temperature on Parameter mRo for Pentane on Carbowax 1500

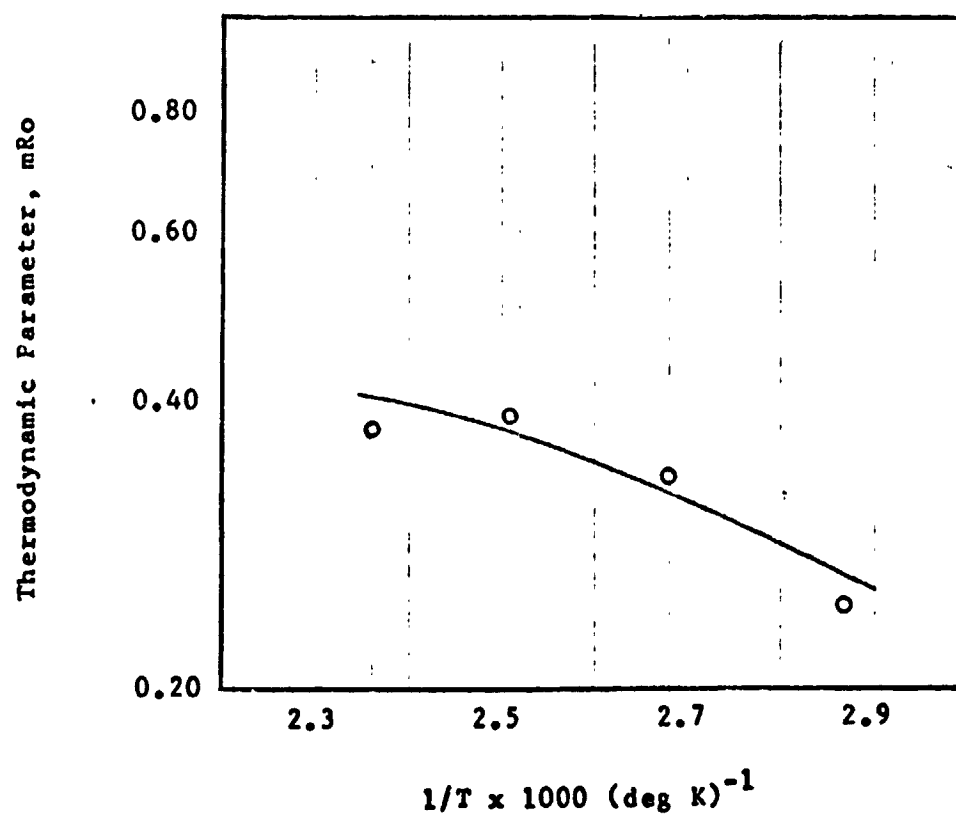


Figure 10 Effect of Temperature on Parameter mRo for Heptane on Carbowax 1500

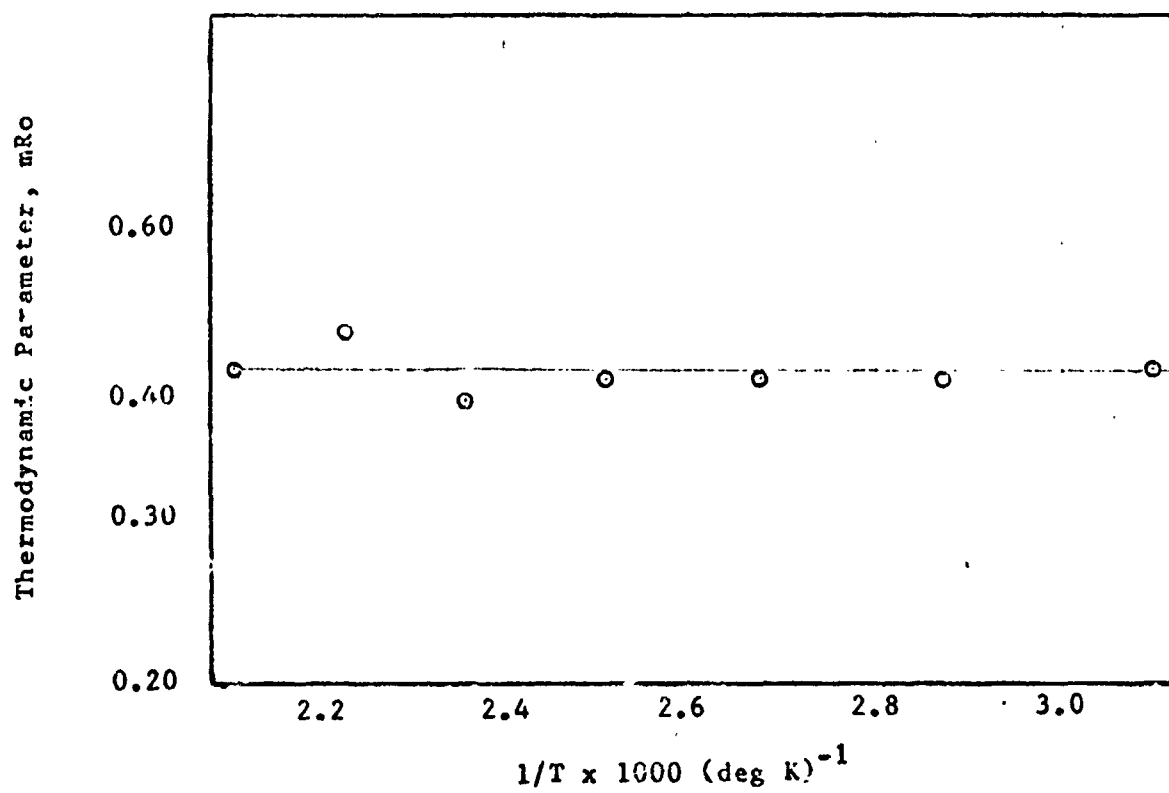


Figure 11 Effect of Temperature on Parameter mR_o for Ethylene on Carbowax 1500

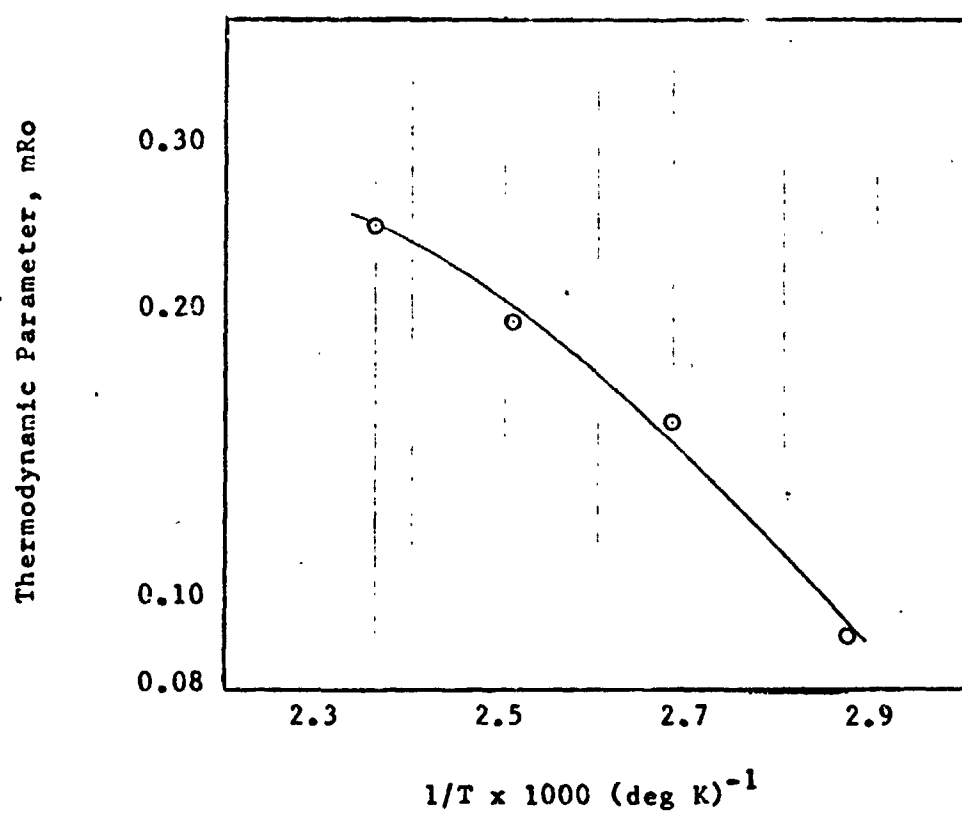


Figure 12 Effect of Temperature on Parameter mRo for Mek on Carbowax 1500

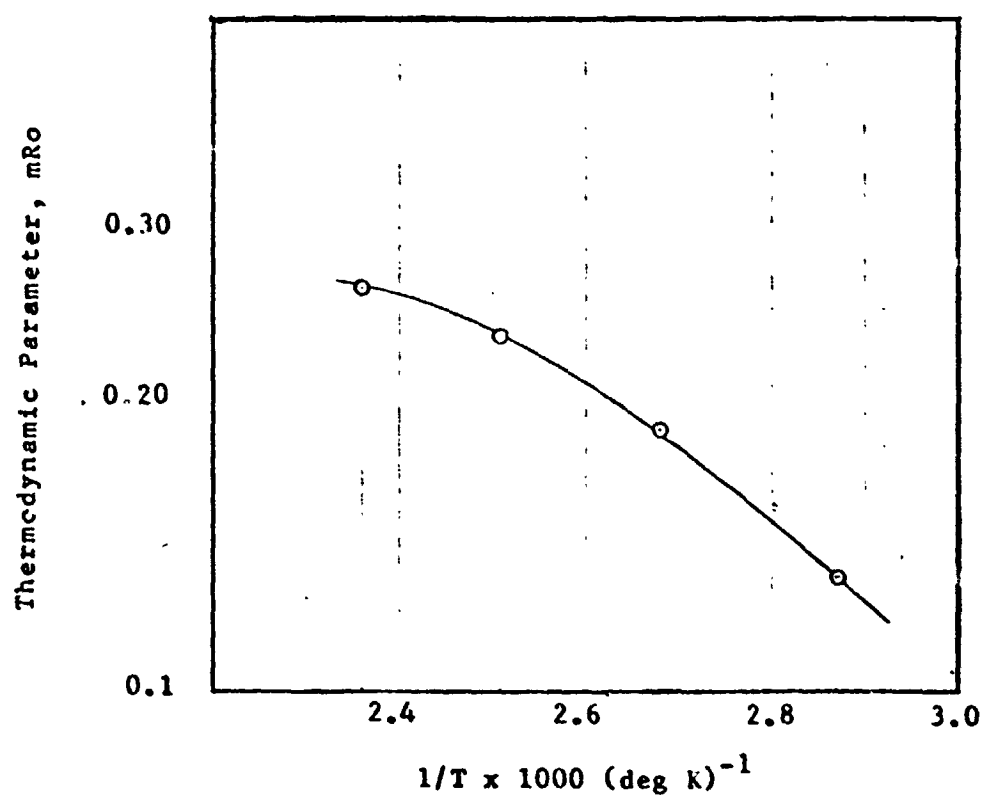


Figure 13 Effect of temperature on Parameter mRo for Acetone on Carbowax 1500

TABLE V

PURE COMPONENT DATAON DESPENTANE (50°, 75°, 100°, 125°)

Temp °C	Sample Size l	Input Peak sec	Flow Rate cc/min	Gas Velocity cm/sec	Peclet No.	N _{tog}	mRo
50°	1.0	10.0	14.6	2.67	986	638600	0.1578
75°	1.0	8.0	21.6	3.98	1380	466400	0.2311
100°	0.2	3.33	22.9	4.45	1394	462200	0.3596
100°	0.5	3.25	22.9	4.45	1394	462200	0.3659
100°	1.0	3.33	22.9	4.45	1394	462200	0.3813
100°	1.0	6.5	27.5	5.26	1671	390700	0.3333
125°	0.5	2.5	23.2	4.73	1349	476300	0.5197

HEPTANE (75°, 100°, 125°)

Temp °C	Sample Size l	Input Peak sec	Flow Rate cc/min	Gas Velocity cm/sec	Peclet No.	N _{tog}	mRo
75°	1.0	8.0	21.6	3.98	1658	391700	0.0431
100°	0.2	11.0	22.3	4.33	1629	398100	0.0806
100°	0.5	11.5	27.5	5.26	2005	328600	0.0751
100°	0.5	8.0	22.6	4.39	1651	393200	0.0823
100°	1.0	7.5	27.5	5.26	2005	326600	0.0801
100°	1.0	8.0	22.6	4.39	1651	393200	0.0799
100°	3.0	6.5	27.5	5.26	2005	328600	0.0795
125°	1.0	3.0	23.0	4.69	1605	403600	0.1459

TABLE VI

BINARY DATA ON DESPentane - Heptane 100° C

	Flow Rate cc/min	Gas Velocity cm/sec	Peclet No.	N _{tog}
Pentane	22.3	4.33	1357	473700
Heptane	22.3	4.33	1629	398100

Wt Fraction Pentane	Wt Fraction Heptane	Input Peak	Pentane mRo	Heptane mRo
.99	.01	3.0	0.3668	0.0827
.90	.10	3.0	0.3668	0.0824
.75	.25	8.0	0.3504	0.0819
.50	.50	7.0	0.3453	0.0822
.25	.75	7.0	0.3504	0.0829
.10	.90	3.0	0.3505	0.0830
.01	.99	3.0	0.3451	0.0830

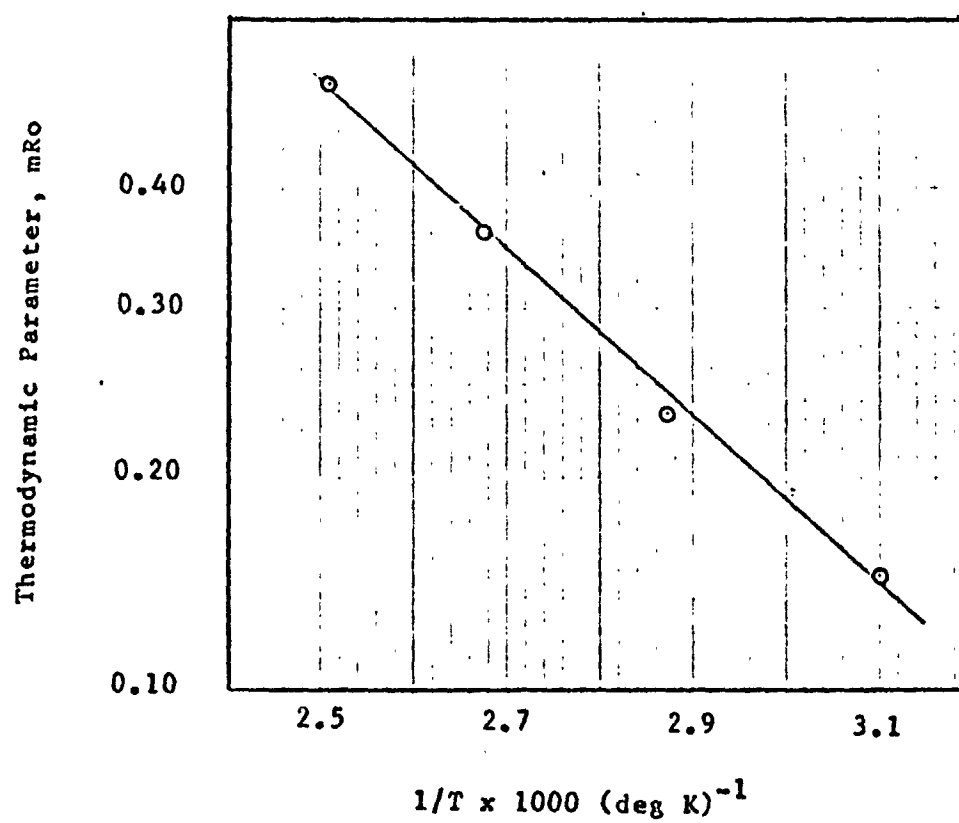


Figure 14 Effect of Temperature on Parameter mRo for Pentane on DES

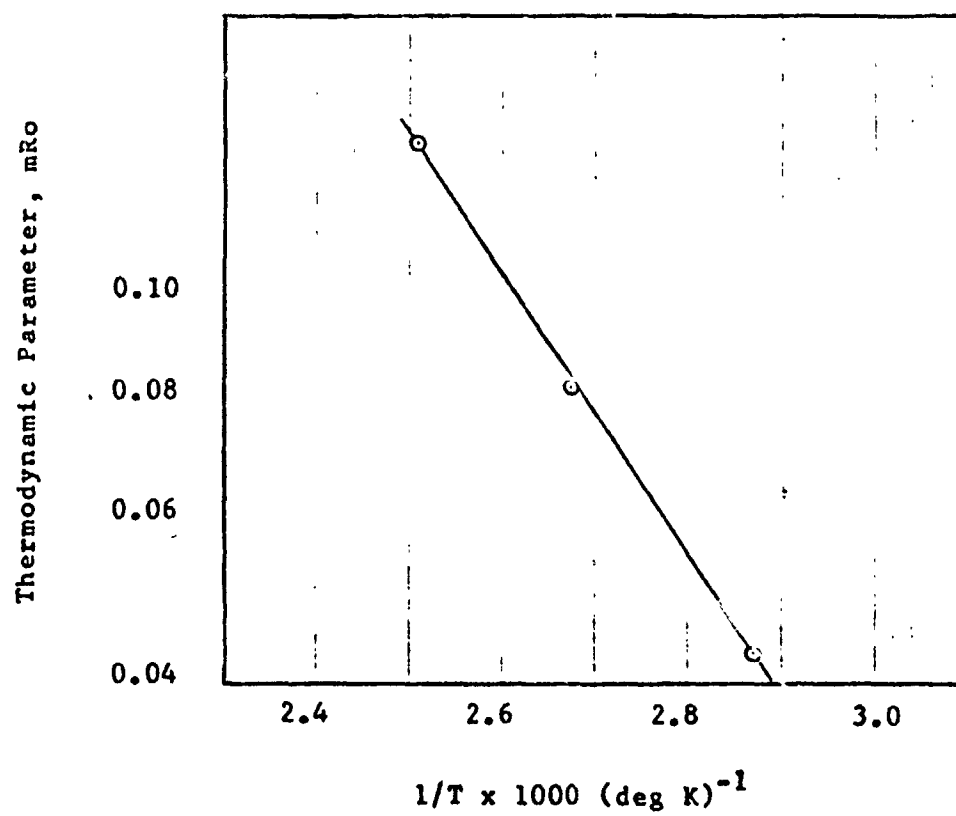


Figure 15 Effect of Temperature on Parameter mRo for Heptane on DES

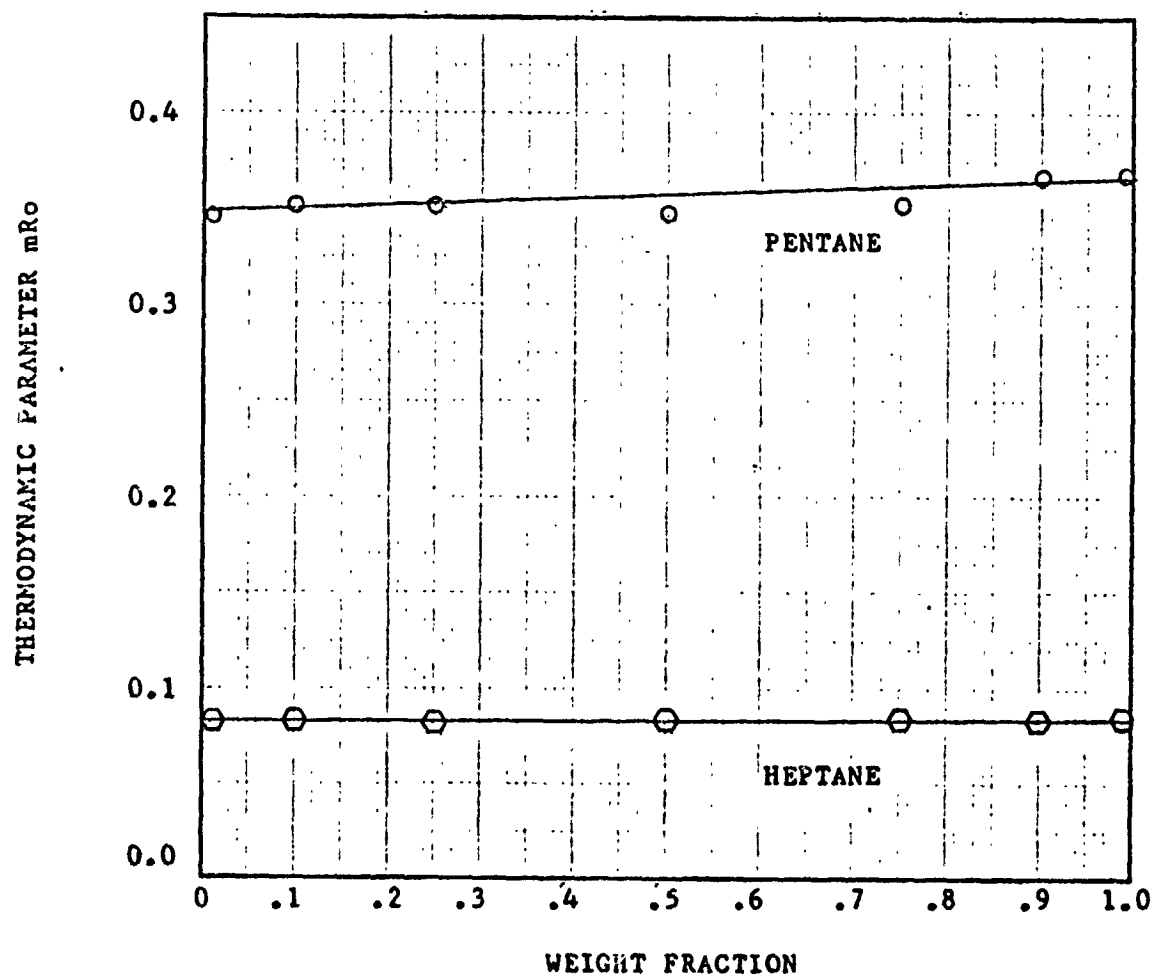


Figure 16 Effect of composition on parameter mRo in binary sample on DES at 100°C.

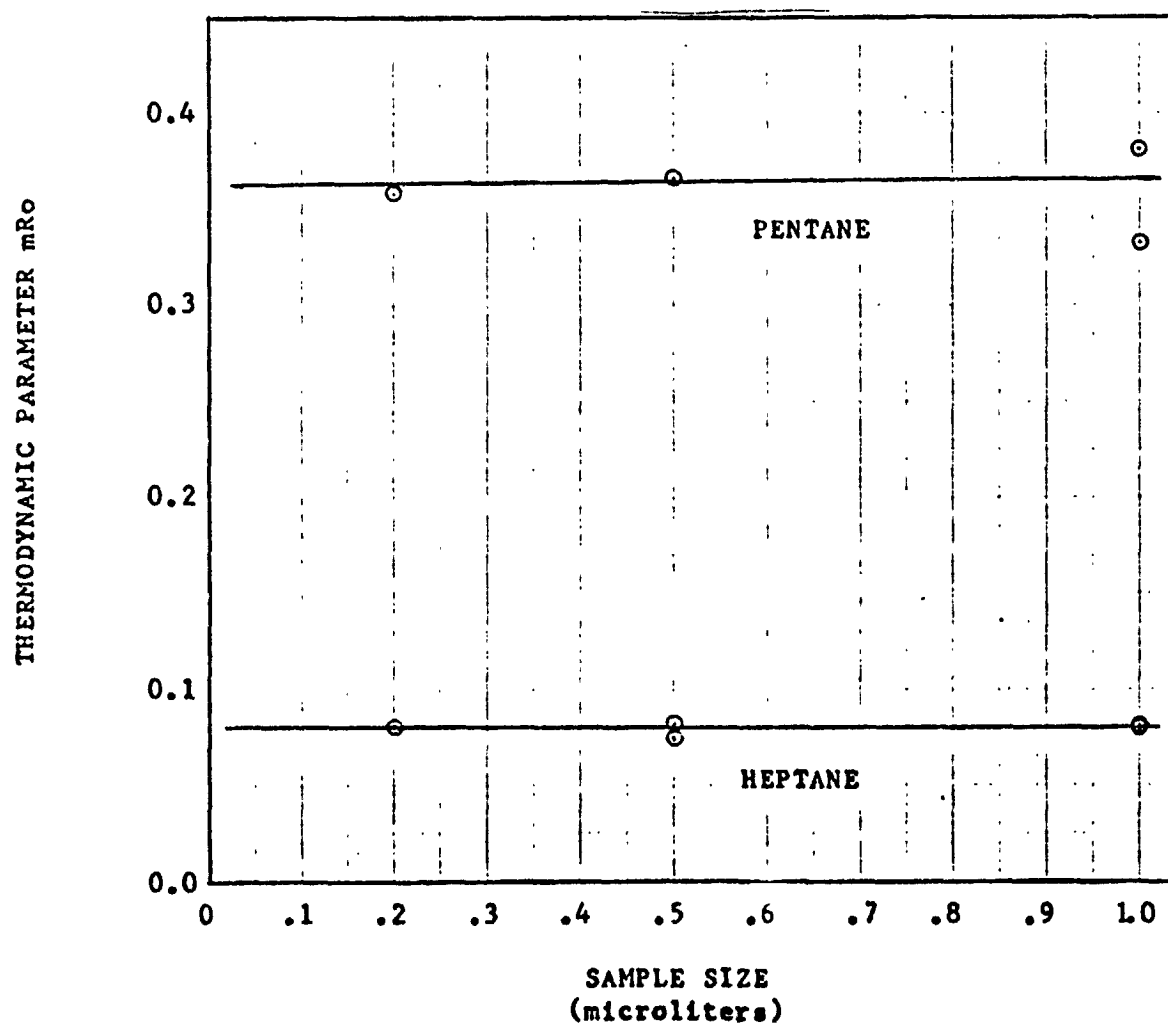


Figure 17 Effect of sample size on parameter mRo in experimental runs on DES at 100° C.

data on C-1500, C-102, and DES are reported in Tables VII, VIII, and IX.

The activation energy of adsorption-desorption can be calculated from the following relation:

$$mRo \propto \exp(-E_a/RT)$$

which has been used to correlate data. Table X lists the activation energies for experimental data on the three columns.

These activation energies are in the same range as the latent heats of condensation for the liquid samples. This observation leads to the conclusion that physical adsorption is the predominant type of adsorption in the columns (Smith, 1970). In physical adsorption the activation energy for adsorption is generally less than 1.0 Kcal/g-mole, while the activation energy of desorption is larger because desorption is normally an endothermic process. This relation is shown mathematically in this equation:

$$E_d = E_a - H_a$$

where H_a , the heat of adsorption is in the same range as the heat of condensation. Thus desorption is the controlling mechanism.

E. Analysis of Data

All of the experimental chromatography was done on three columns, the chromosorb-102 which is packed with a microporous polymeric bead, and the carbowax 1500 and DES columns which are relatively nonporous. Table XI compares the characteristics of the first two columns to those of the DES column, which was acquired this year for the purpose of separating pentane and heptane using a nonporous adsorbent. It is desirable to have

TABLE VII

DIMENSIONLESS MOMENTS ON C-1500

Acetone		Input Pulse	Output Pulse
75°	1	1.75	10.75
	2	2.76	4.80
	3	13.80	27.20
Pentane			
75°	1	1.48	5.62
	2	.946	1.13
	3	2.20	1.93
Heptane			
75°	1	2.85	8.20
	2	6.85	7.34
	3	22.90	43.10
Mek			
75°	1	2.55	15.2
	2	8.09	15.3
	3	71.60	153.0
100°	1	2.04	9.83
	2	5.02	4.14
	3	33.9	18.8
125°	1	2.02	8.29
	2	4.43	4.44
	3	29.0	23.6
150°	1	1.55	7.0
	2	1.74	3.54
	3	6.55	17.3
Ethylene			
50°	1	.114	3.72
	2	.0043	.282
	3	.0006	.319

TABLE VII (cont)

Ethylene		Input Pulse	Output Pulse
75°	1	.121	3.81
	2	.0083	.302
	3	.0029	.395
100°	1	.132	3.81
	2	.0073	.334
	3	.0021	.453
100° syringe	1	4.76	9.07
	2	8.45	9.18
	3	37.70	37.70
125°	1	.115	3.62
	2	.0069	.385
	3	.00209	.599
150°	1	.125	3.94
	2	.00422	.372
	3	.00061	.536
175°	1	.121	3.52
	2	.0042	.280
	3	.0009	.352
200°	1	.128	3.74
	2	.005	.356
	3	.001	.488

TABLE VIII

DIMENSIONLESS MOMENTS ON C-102

Mek		Input Pulse	Output Pulse
150°	1	.755	46.4
	2	.568	17.1
	3	.135	91.4
175°	1	.845	29.1
	2	.627	4.93
	3	.122	13.9
200°	1	1.0	13.7
	2	.34	2.04
	3	.432	5.76

TABLE IX

DIMENSIONLESS MOMENTS ON DES

Pentane		Input Pulse	Output Pulse
50°	1	.543	7.94
	2	.133	.236
	3	.0597	.103
75°	1	.633	6.11
	2	.194	.365
	3	.121	.295
100° .2 μ l	1	.185	4.05
	2	.0073	.071
	3	.0009	.038
100° .5 μ l	1	.187	4.01
	2	.0104	.0524
	3	.0022	.0183
100° 1 μ l	1	.215	3.99
	2	.0162	.0815
	3	.0046	.0366
100° 1 μ l	1	.625	4.75
	2	.228	.344
	3	.237	.389
125°	1	.198	3.21
	2	.0214	.0509
	3	.00759	.0194
Heptane			
75°	1	.655	24.86
	2	.221	.824
	3	.168	.232
100° .2 μ l	1	.762	14.70
	2	.275	.478
	3	.287	.312
100° .5 μ l	1	1.28	15.73
	2	.910	1.56
	3	1.35	2.91

TABLE IX (cont)

Input Pulse			Output Pulse
100° .5 μ l	1	.675	13.80
	2	.233	.542
	3	.218	.367
100° 1 μ l	1	.782	14.29
	2	.413	.518
	3	.574	.368
100° 1 μ l	1	.696	14.28
	2	.269	.494
	3	.273	.344
100° 3 μ l	1	.824	14.47
	2	.496	.726
	3	.616	.716
125° 1 μ l	1	.216	8.11
	2	.0217	.113
	3	.0079	.024

TABLE X

ACTIVATION ENERGIES OF ADSORPTION (KCal/Mole)

Component	C-1500	C-102	DES
Pentane	1.34	11. (1)	4.03
Heptane	2.68	15. (1)	6.64
Acetone	3.73 (75°-100°) 1.59 (125°)	6. (2)	-
Mek	2.88	7.07	-
Ethylene	~ 0	4.0 (28°C) 1.5 (175°)	-

(1) Meisch (1973)

(2) Keba and Woodrow (1972)

TABLE XI

COLUMN CHARACTERISTICS

	<u>CHROMOSORB 102</u>	<u>CARBOMAX 1500</u>	<u>DES</u>
Length	100 cm	100 cm	100 cm
Outside Diameter	.318 cm	.318 cm	.635 cm
Inside Diameter	.22 cm	.22 cm	.555 cm
Mesh	60/80	60/80	60/80
Particle Size	.025/.0177 cm	.025/.0177 cm	.025/.0177 cm
Composition	Microporous Styrene-divinyl Benzene Polymers	Polyethylene Glycol 20% by Weight on Chromosorb P (diatomaceous earth)	Di-2-ethylhexyl sebacate 20% by Weight on Chromosorb P
Temperature Range	Room-250° C	Room-225° C	Room-125° C
Application	Separation of low molecular weight very polar sub- stances	Separation of high boiling polar com- pounds	Separation of hydrocarbons from C ₄ and up

an array of columns with different characteristics so that all possible physical phenomena can be observed, leading to appropriate general models.

Previous workers have gathered a great deal of data for ethylene, pentane, heptane, and acetone on C-102 and C-1500 (Meisch, 1973; Benoit, 1971). Comparison of these data to the equilibrium adsorption model simulations showed reasonable agreement in most cases with some obvious deviations. In general the data on the C-1500 column were more accurately modeled than those on C-102. On the C-102 column, more spreading was observed than was predicted by the model. It has been postulated that this spreading is due to pores in the packing particles not accounted for in the model. New data has served to clarify the situation.

The largest deviation occurred when ethylene was injected onto C-102 using the Carle minivalve. In this situation a 100 μ l. sample was injected as a sharp concentrated pulse with a duration of less than a second. The model predicted a correspondingly sharp output pulse while the actual output was a very wide low pulse with tremendous tailing. These results were shown in Figure 1.

If porous intraparticle effects were the cause of the spreading then the nonporous C-1500 should show somewhat different behavior. When ethylene was used on this column the behavior was no different. A sharp input pulse was converted to a wide output, as is shown in Figure 18. When the concentration of

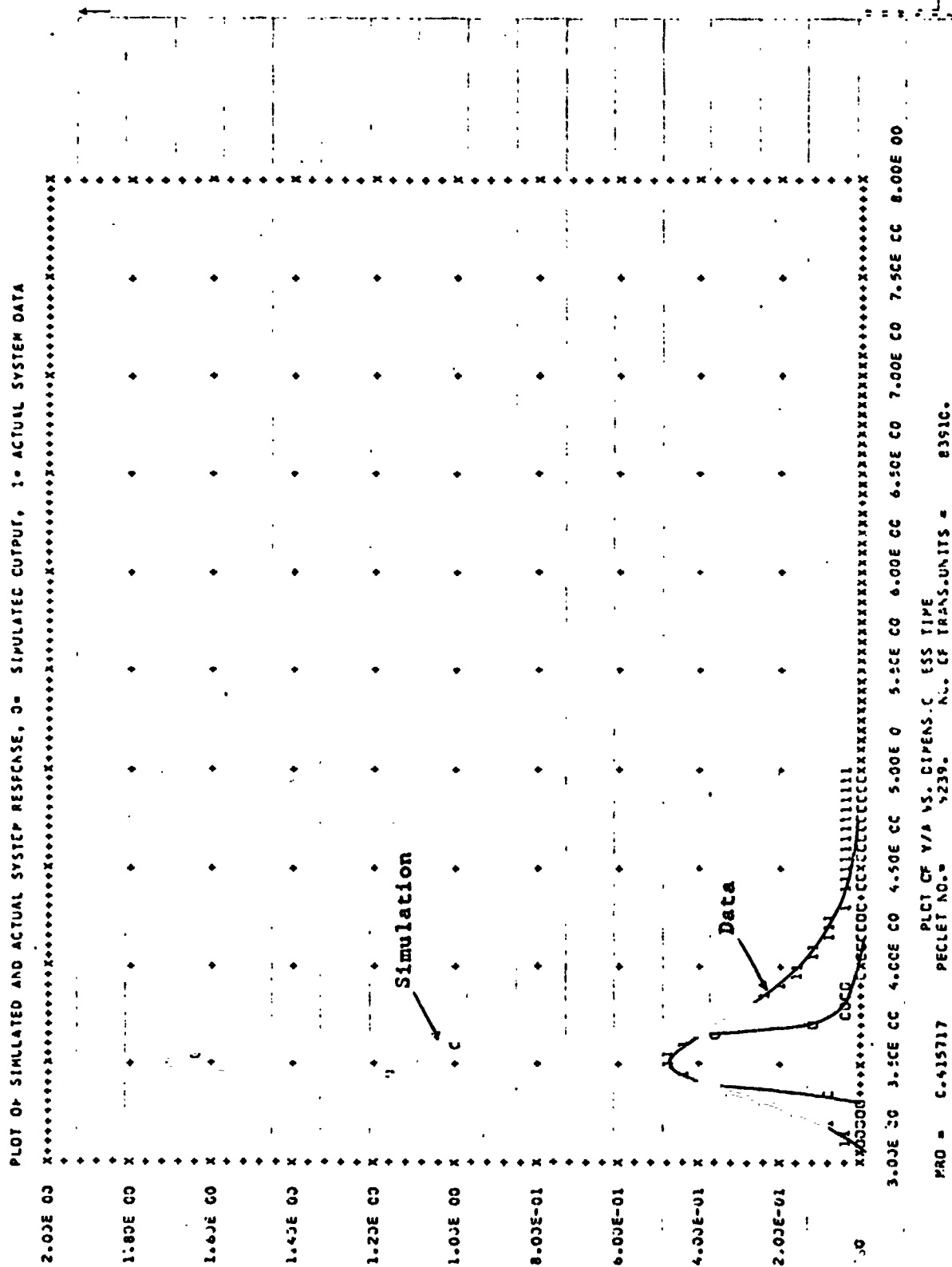


Figure 18 Simulated and Actual Chromatographic Data for Ethylene on C-1500

ethylene was computed it was found that the peak mole fraction was nearly 0.20 in the input pulse and less than 0.04 in the output. The equilibrium adsorption model is not valid for large sample concentrations because it is simplified for small values of y . The exact equation

$$(1 + 1/mRo) \partial y / \partial \theta = (1/Pe) \partial^2 y / \partial z^2 - 1/(1 - y) \partial y / \partial z$$

is simplified to a linear equation by assuming $1/(1 - y) = 1$ to yield:

$$(1 + 1/mRo) \partial y / \partial \theta = (1/Pe) \partial^2 y / \partial z^2 - \partial y / \partial z$$

Moreover the model is based on a linear isotherm which may be a poor approximation for large concentrations. A nonlinear Langmuir type isotherm might better describe the situation.

To determine the effect of sample size on this observed behavior, the ethylene was injected at lower sample pressure and the helium flow rate was increased. But the ethylene concentration could not be reduced enough to affect the behavior of the column. The Carle minivalve can not be used to vary sample size over a large range. A gas tight syringe was used to get smaller ethylene concentrations. Figure 19 shows the results of this experiment. Using a wide input with low peak sample mole fraction, the output is extremely well modeled. The non-linearity appears to be composition dependent.

Pentane and heptane on C-102 also have more spreading than the model predicts. When they were injected as a binary mixture another deviation was discovered. The value of mRo depended on the composition of the sample (Heisch, 1973). To discover

PLUT GP SIMULATED AND ACTUAL SYSTEM RESPONSE, O= SIMULATED OUTPUT, I= ACTUAL SYSTEM DATA

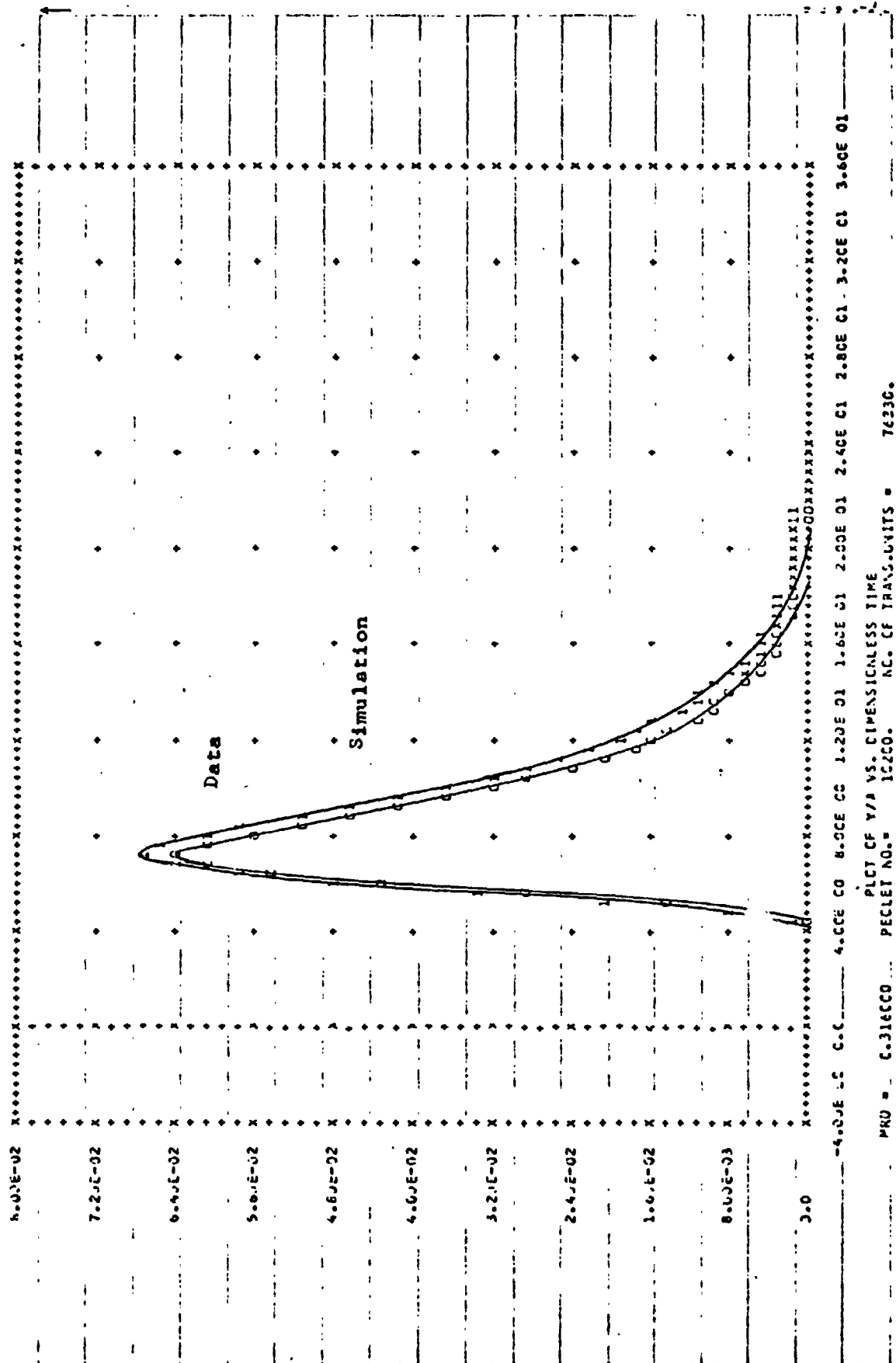


Figure 19 Simulated and Actual Data for Syringe Injected Ethylene on C-1500

whether this variable mR_o was due to the porosity of the column packing, it was attempted to separate the mixture on the nonporous C-1500 for comparison. No separation was possible so the question remained unanswered. Column manufacturer's data indicated that a mixture of acetone and mek would be more likely to separate on the carbowax column. When this mixture was tested, separation was minimal so it was decided to get another nonporous column that would separate low molecular weight hydrocarbons.

The column chosen for these conditions was the DES column, a diatomaceous earth substrate covered with di-2-ethylhexyl sebacate. The data from this column were extremely well modeled by the equilibrium adsorption model. Figure 20 compares the simulation to data from this column. When binary mixtures of pentane and heptane were used on the DES column it was found that linear superposition predicted the actual results quite well. The parameter mR_o was not a strong function of composition as is shown in Figure 21. Furthermore it was found that mR_o was independent of sample size for this system.

It was postulated that the composition dependence of mR_o was due either to interaction between the two sample components or to the fact that the total amount of a component varied in samples of different composition. For example if the total sample was $2.0 \mu\text{l}$ the amount of heptane in a 0.1 heptane - 0.9 pentane mixture would be only equivalent to about $0.2 \mu\text{l}$ compared to $1.8 \mu\text{l}$ for a 0.9 heptane - 0.1 pentane mixture.

To clarify the behavior, pure heptane was injected onto C-102 with sample sizes varying from 0.2 to $3.0 \mu\text{l}$. For these

PLUT CF SIMULATED AND ACTUAL SYSTEM RESPONSE, C= SIMULATED OUTPUT, 1= ACTUAL SYSTEM DATA

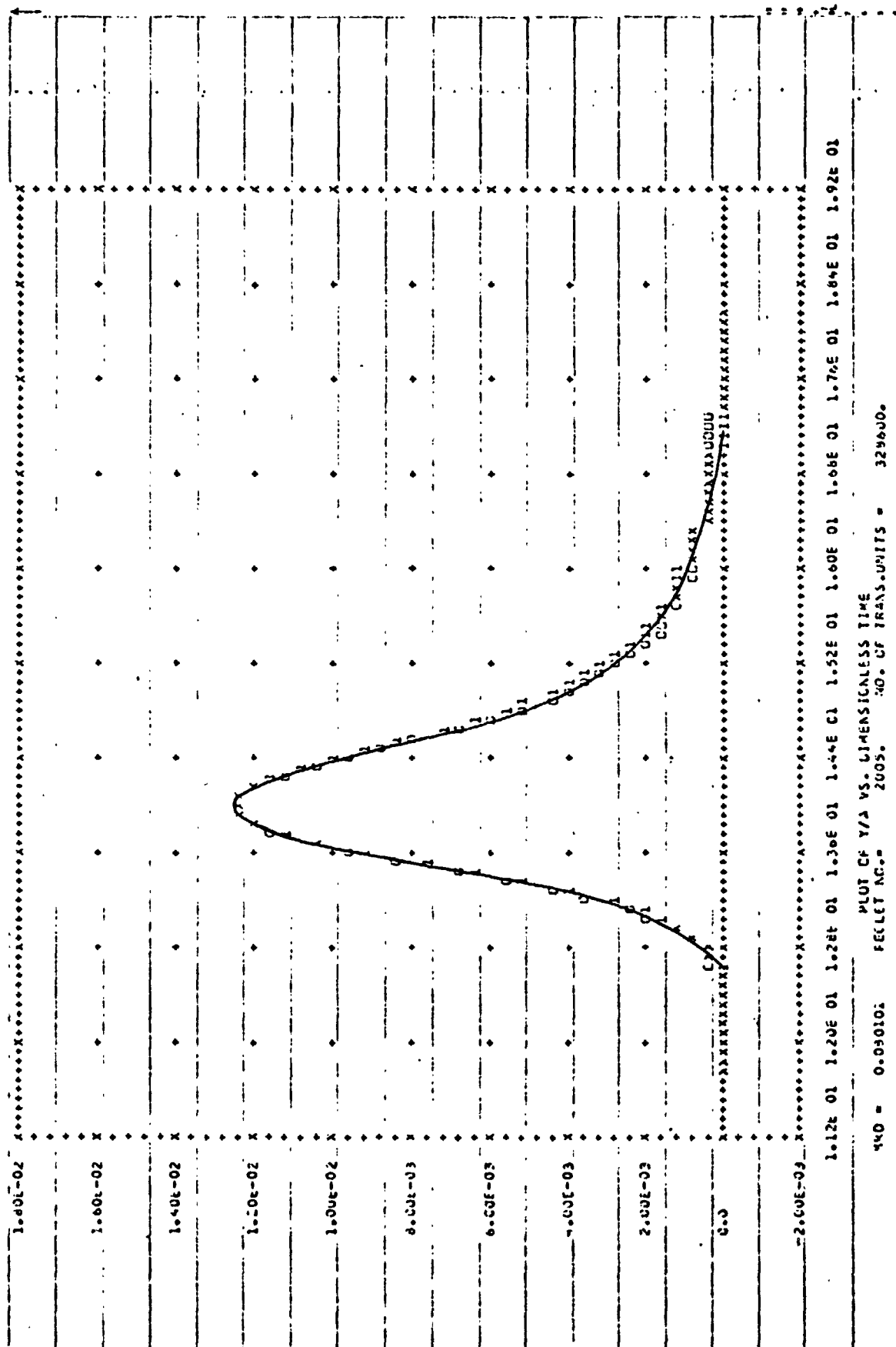


Figure 20 Simulated and Actual Data for Heptane
on DES

runs, the value of mR_o was found to be a strong function of sample size (ie. mole fraction in the carrier stream). Figure 22 compares the variation of mR_o with sample size for pure heptane runs to the variation with binary sample runs. The variation is similar. Any differences are probably due to the fact that the binary runs were made with wider input pulses, causing peak sample concentrations in the carrier gas to be somewhat less than in the pure component runs of the same sample size. It was concluded that interactions between pentane and heptane had a negligible effect on mR_o , and that any composition dependence was primarily due to the actual composition of the component in the gas stream.

F. Incorporation of the Langmuir Isotherm into the Model, And a Solution by Orthogonal Collocation

When the behavior of ethylene on C-102 was discussed, it was stated that a nonlinear isotherm might yield a more accurate model. This is also believed to be the case for pentane and heptane on chromosorb 102. A nonlinear isotherm of the Langmuir type may possibly explain the deviations in both situations.

The Langmuir isotherm gives the following relation between the adsorbed phase and mobile phase mole fractions (Brunauer, 1943).

$$x = K_y / (1 + K_y)$$

This equation is compared to the linear isotherm in Figure 23. For small concentrations the isotherm has nearly linear behavior. For large concentrations, the amount that can be adsorbed becomes proportionally less and finally reaches a maximum value. Larger

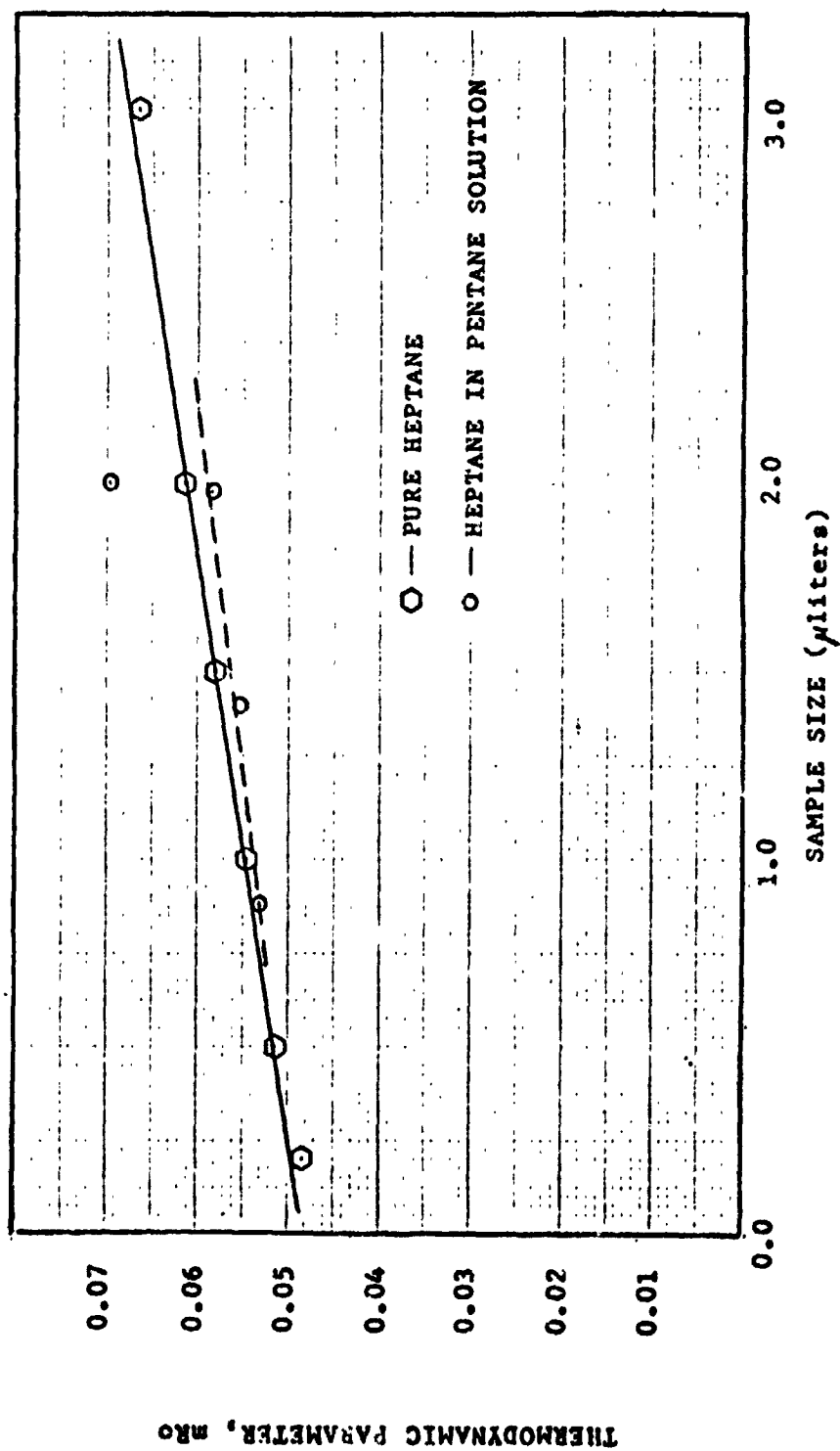


Figure 22 Effect of Sample Size On mRo , For Heptane On Chromosorb 102

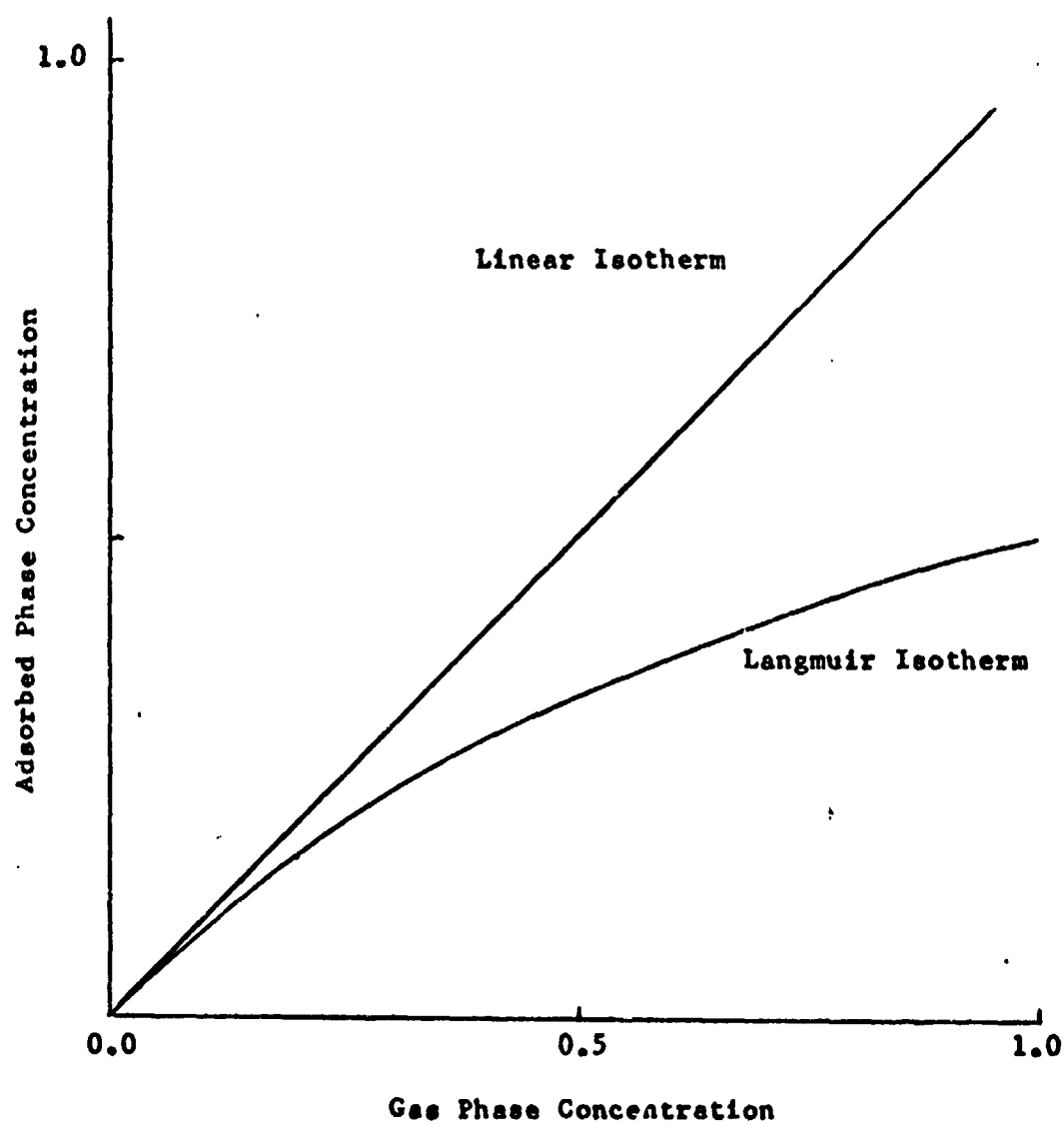


Figure 23 Comparison of the Linear and Langmuir Isotherms

values of K make the isotherm nonlinear at lower mobile gas phase concentrations.

The nonlinearity would have the following effect on the behavior of the column. Large samples entering the column would be adsorbed proportionally less in zones of high concentration than in low. As a result large samples would begin to elute sooner than small samples and would be more spread. The quantitative effects of the isotherm on spreading and mR_0 can only be found by solving the model.

This model takes the following form: (Appendix E - derivation)

$$(1 + 1/mR_0(1 + Ky)^2) \partial y / \partial \theta = (1/Pe) \partial^2 y / \partial z^2 - 1/(1-y) \partial y / \partial z$$

Comparing this equation to the equilibrium adsorption model, the only difference is the term $(1 + Ky)^2$ multiplying mR_0 . In effect, the parameter mR_0 becomes a variable dependent on composition y . The dependence becomes stronger as K increases. The average value of $mR_0(1 + Ky)^2$ increases with sample concentration. This is the observed behavior in experimental data. The amount of tailing predicted with this model can not be estimated without solving the equation.

The equation must be solved numerically because it is complicated and nonlinear. Based on recent research, finite difference methods could be used but would probably take a prohibitive amount of computer time (Pfeiffer, 1972; Woodrow, 1974). The method of orthogonal collocation as developed by Woodrow (1974), has been used to advantage in some problems encountered in chromatography. This method of solution was adapted to the Langmuir

isotherm problem with the same trial function and set of orthogonal polynomials used by Woodrow. The details concerning the formulation of the solution are in Appendix F.

The first set of solutions was completed for the equation with K set to zero. The term $1/(1-y)$ was set equal to 1.0 and the equation reduced to the equilibrium adsorption model with a linear isotherm. Figures 24 through 26 show the results with 5, 7, and 15 collocation points. The solutions get progressively closer to the exact solution using convolution, which is shown in Figure 27. However, large oscillations appear on either side of the main peak in the seventh and fifteenth order approximations. Even with 15 collocation points the main peak is much wider and shorter than the exact solution. In all cases however the peak is predicted to occur at the proper time.

Knowing the limitations of the problem solutions calculated by the method as it is currently formulated, it was decided to solve the equation with the term $1/(1-y)$ included and with a Langmuir constant K of 100, 200, and 400. The results of these solutions with 15 collocation points are shown in Figures 28 through 30. With the system parameters kept the same as the other runs, these solutions are compared to the case with K equal to zero. As K becomes larger, corresponding to increasing non-linearity in the isotherm, the peaks elute at earlier times and the amount of tailing appears to increase. Since the solutions are not quantitatively accurate, one can say only that they confirm qualitatively the expectations one has with the addition of the Langmuir isotherm to the model.

PE = 9781
MRO = 0.0611
K = 0.0
N = 3

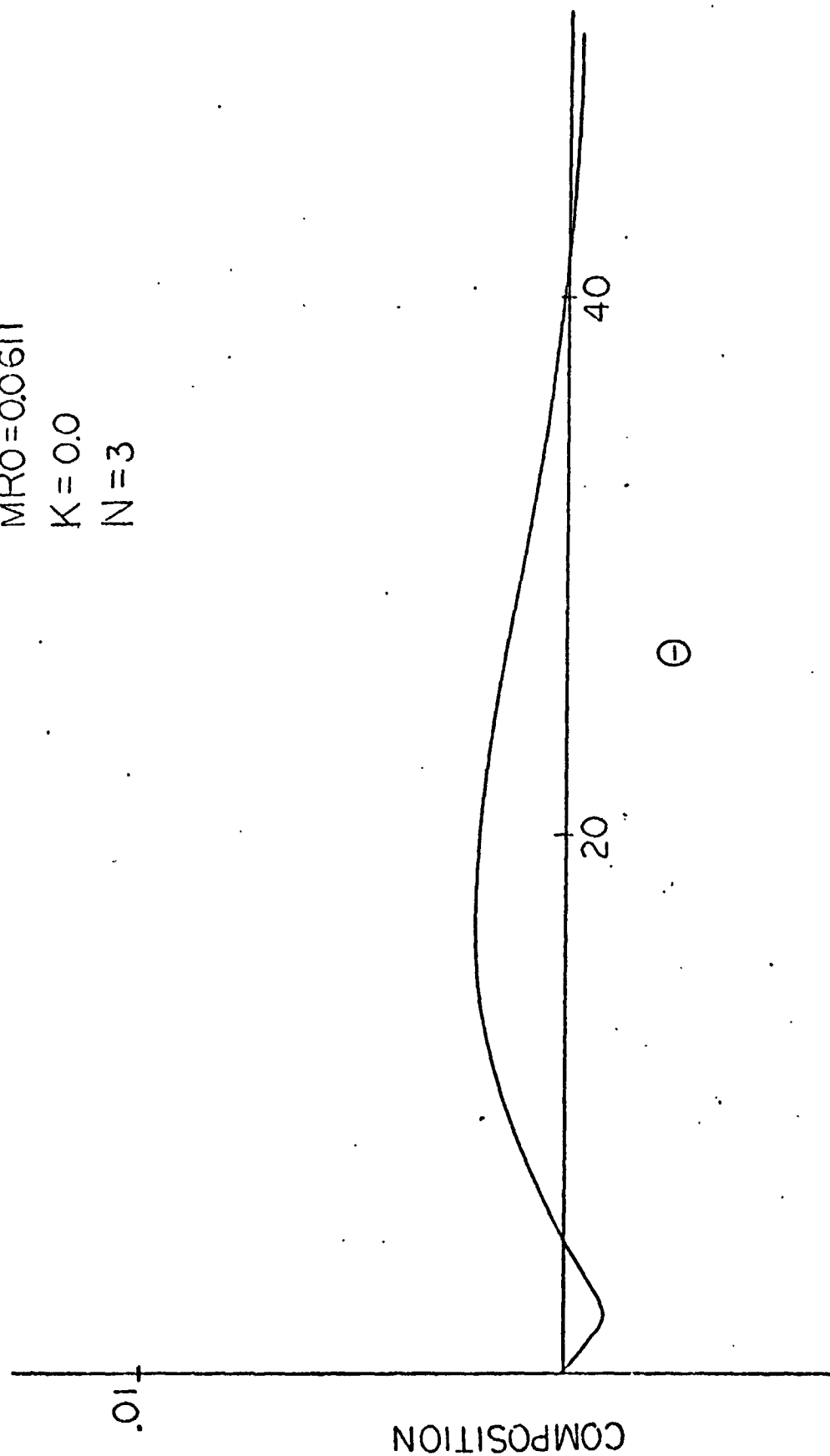


Figure 24 Orthogonal Collocation Solution of the Equilibrium Adsorption Model Using 3 Points

$PE = 9781$
 $MRO = 0.0611$
 $K = 0.0$
 $N = 7$

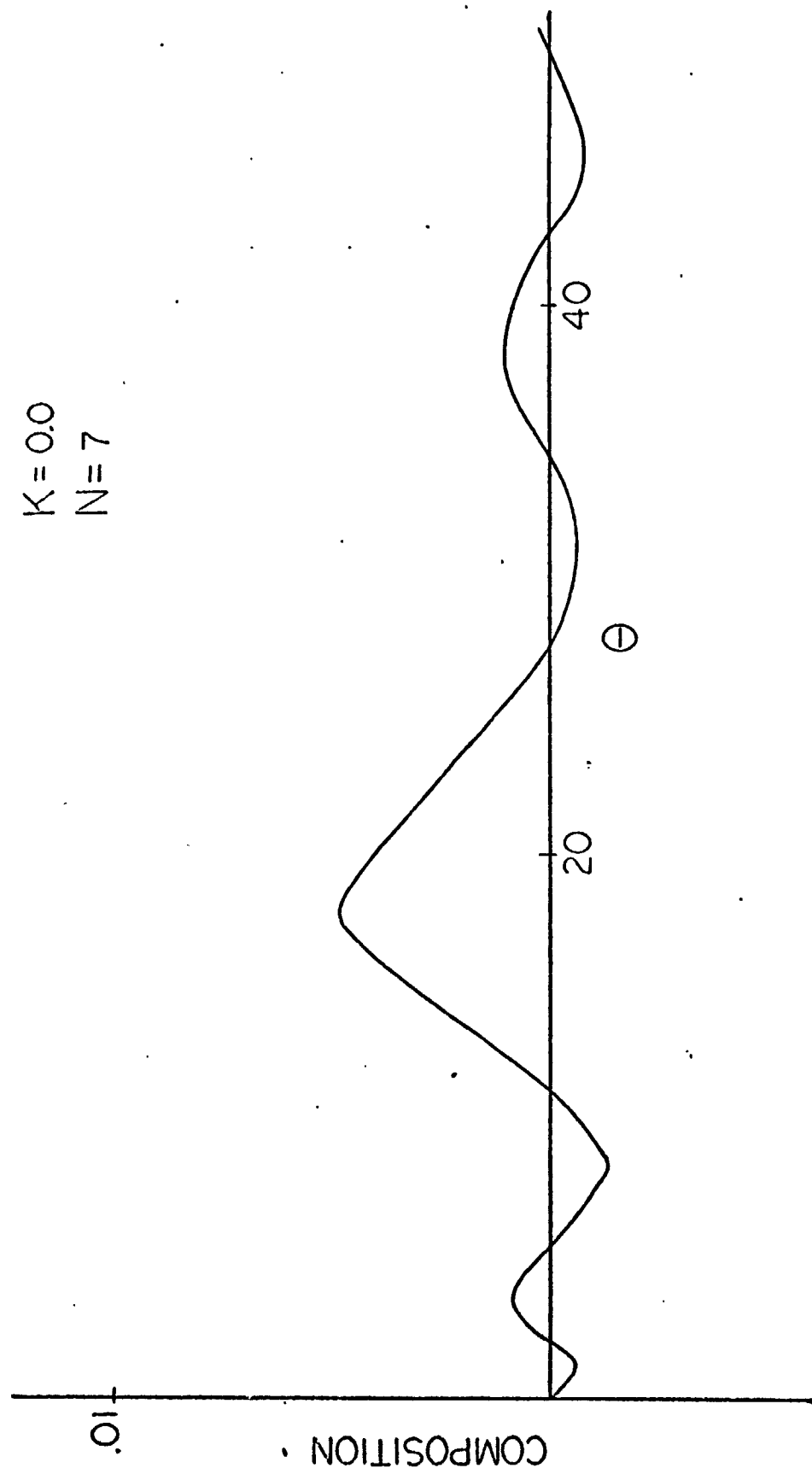


Figure 25 Orthogonal Collocation Solution of the Equilibrium
 Adsorption Model Using 7 Points

PE = 9781
MRO = 0.0611
K = 0.0
N = 15

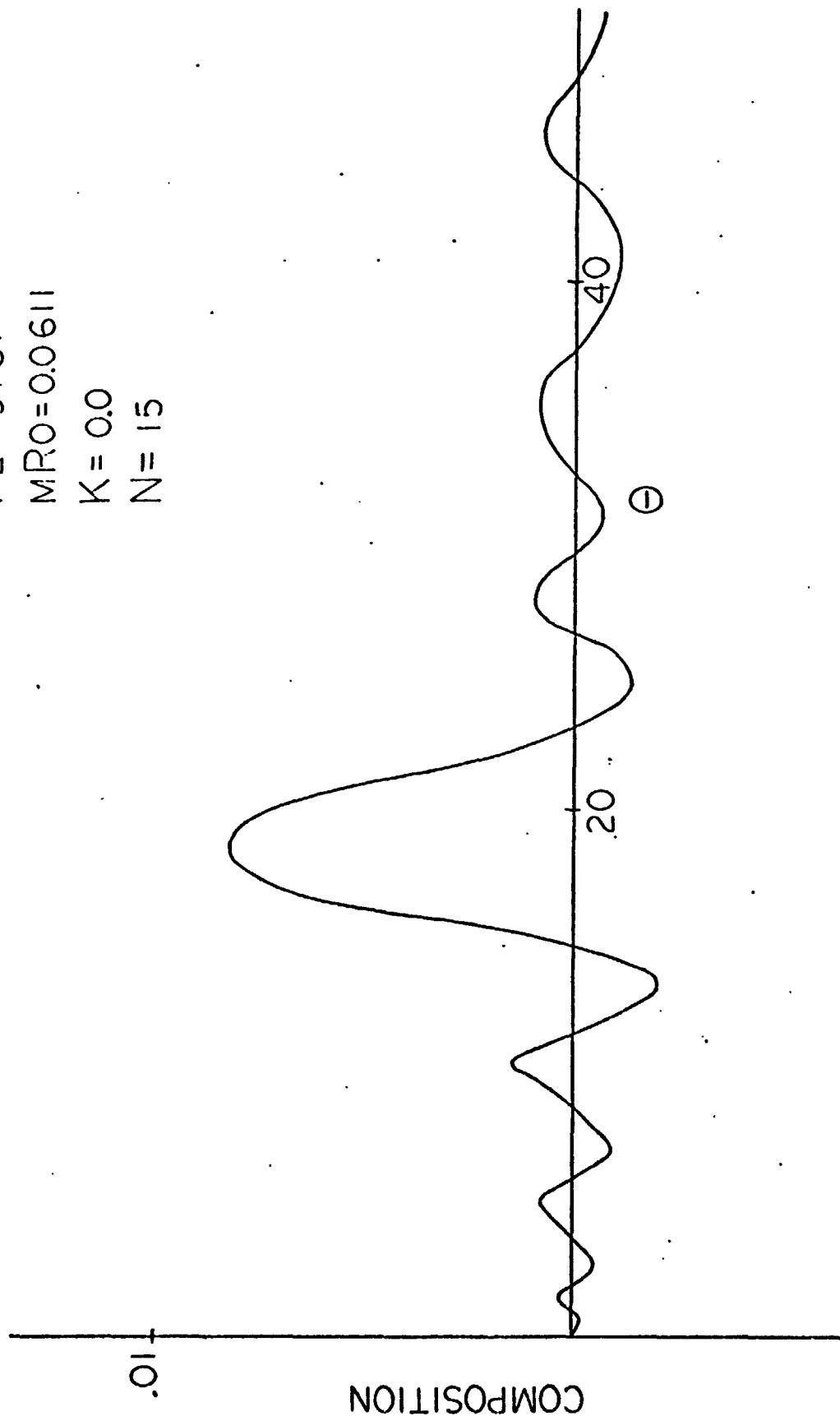


Figure 26 Orthogonal Collocation Solution of the Equilibrium Adsorption Model Using 15 Points

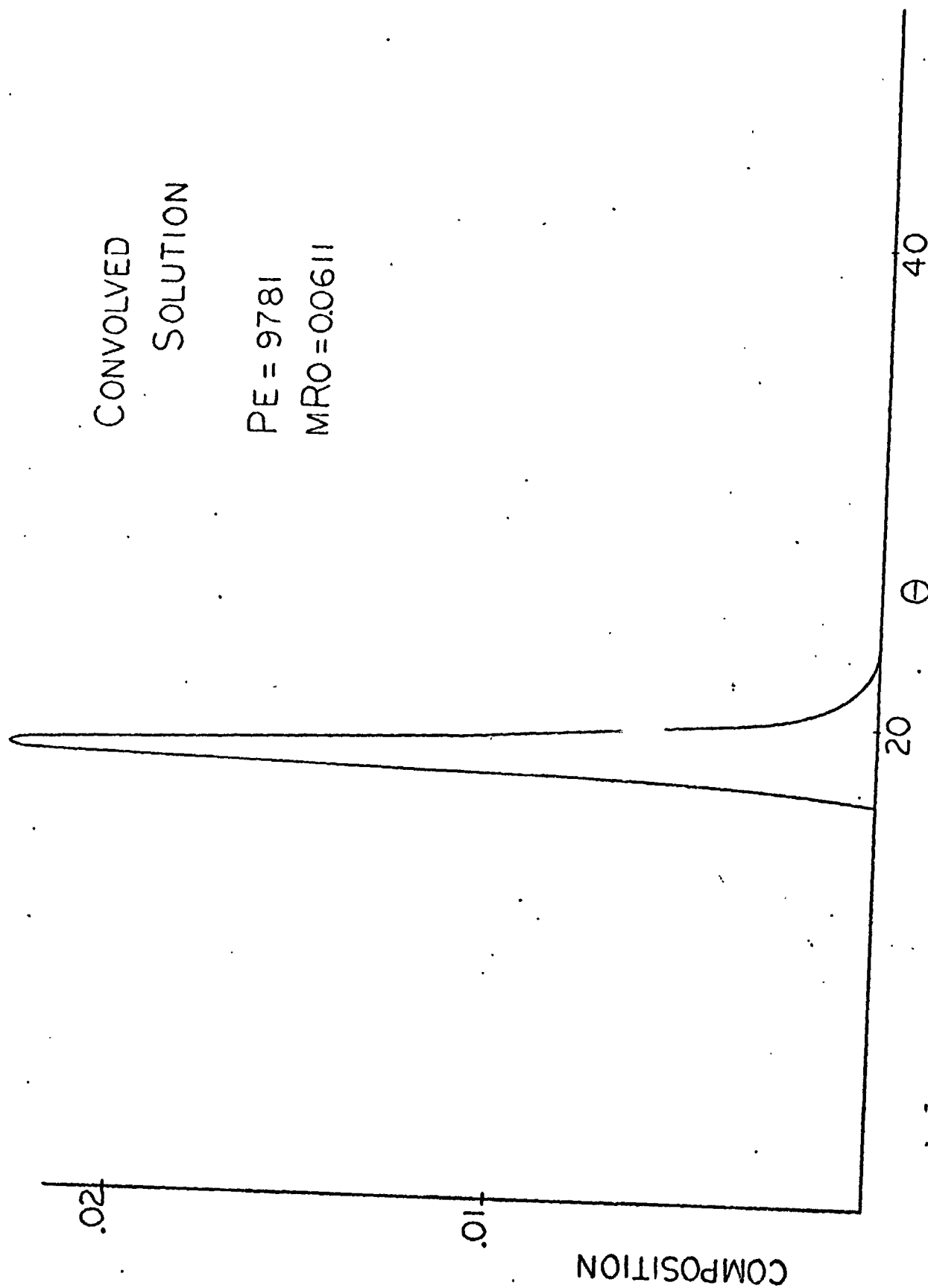


Figure 27 Exact Solution of the Equilibrium Adsorption Model Using Convolution

PE = 9781
MRO = 0.0611
K = 100
N = 15

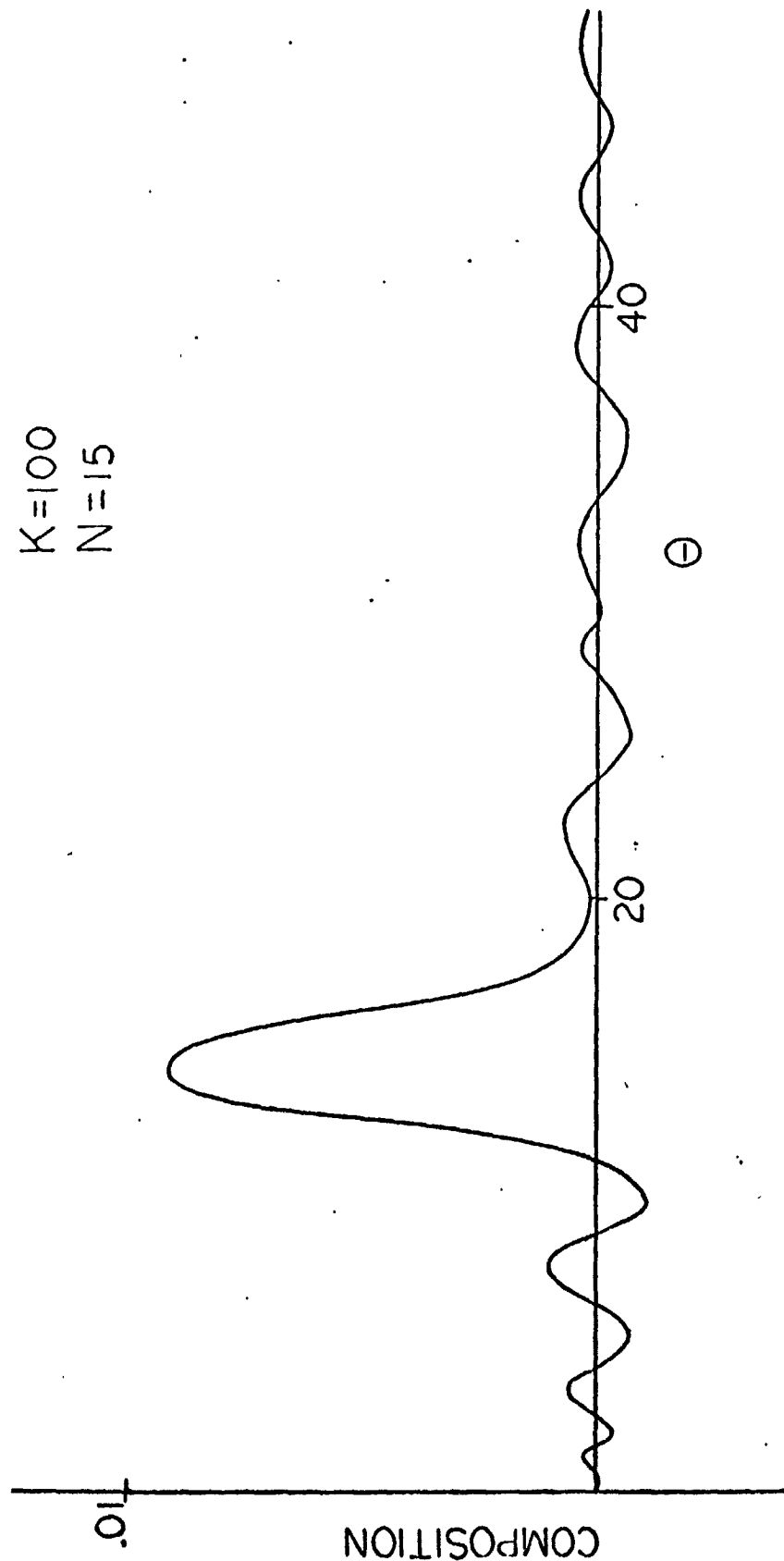


Figure 28 Orthogonal Collocation Solution of the Langmuir Isotherm Model with $K = 100$

$PE = 9781$
 $MRO = 0.0611$
 $K = 200$
 $N = 15$

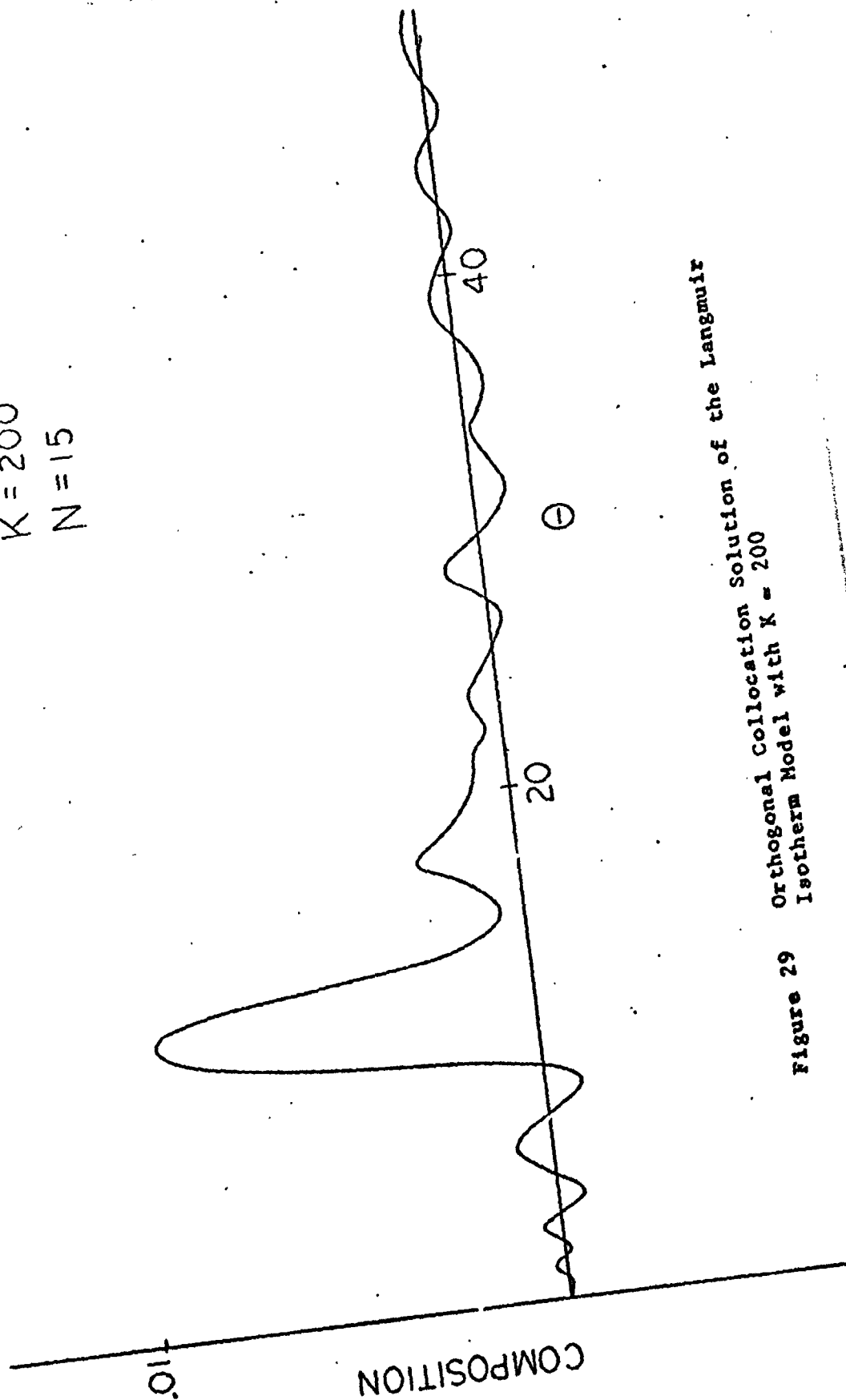


Figure 29 Orthogonal Collocation Solution of the Langmuir
 Isotherm Model with $K = 200$

$PE = 9781$
 $MRO = 0.0611$
 $K = 400$
 $N = 15$

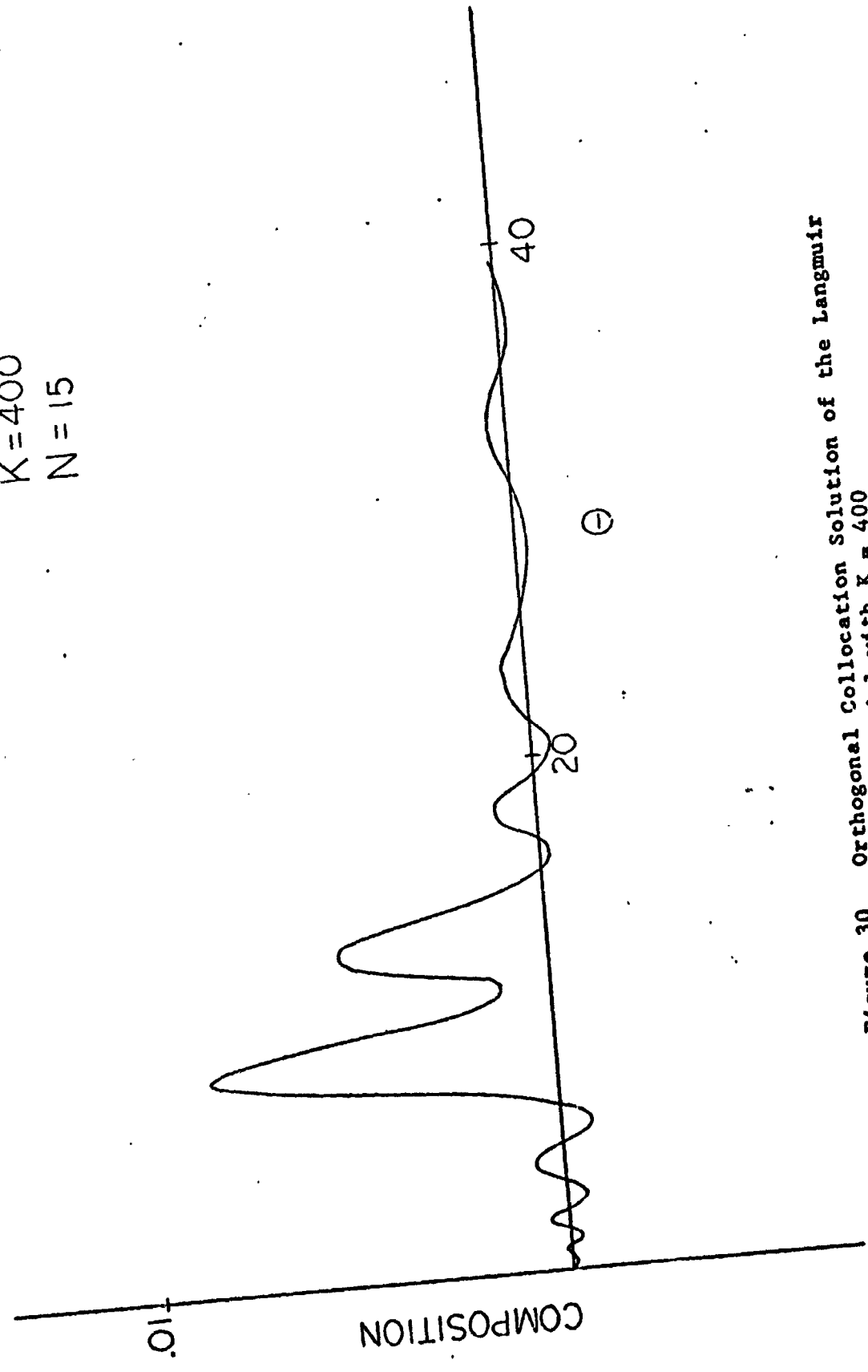


Figure 30 Orthogonal Collocation Solution of the Langmuir
 Isotherm Model with $K = 400$

The characteristics of the collocation method as applied in problem were examined by performing an eigenanalysis on the system of ordinary differential equations resulting from the collocation procedure. The parameter mRo was varied from 100 to 0.01 in the analysis and changes in eigenvalues were noted. The results for three collocation points are presented in Table XII.

TABLE XII

Eigenanalysis for Three Collocation Points

mRo	Eigenvalue	
	Real Part	Imaginary Part
100	-1.43	0.0
	-0.883	1.41
	-0.883	-1.41
10	-1.31	0.0
	-0.811	1.41
	-0.811	-1.41
1	-0.724	0.0
	-0.446	0.773
	-0.446	-0.773
0.1	-0.132	0.0
	-0.0811	0.141
	-0.0811	-0.141
0.01	-0.0143	0.0
	-0.0088	0.0153
	-0.0088	-0.0153

In all cases the values of the real parts of the eigenvalues are negative. This implies that the solutions will be stable. As the parameter mRo decreases however, the real part of the eigenvalue approaches zero which indicates less damping of oscillations and relatively less stability.

If the value of mRo is set very high, the model reduces to the problem of pure convection. Woodrow (1974) has solved this equation using collocation. The solutions proved to be quite stable with little oscillation. Eigenanalysis predicts greater oscillation for low values of mRo and this was observed. It is reasonable to expect that a better formulation for the small mRo problem exists; perhaps a different trial function or set of polynomials would solve the problem more accurately. Little work has been done in this area.

V. CONCLUSIONS AND RECOMMENDATIONS

From the analysis of new experimental data and observations documented in this report, the following conclusions are reached:

1. Modifications to the experimental equipment have improved its versatility and the accuracy of the data it provides.

2. Changes in the data analysis programs and techniques for using them have added new tools to the understanding of experimental results.

3. The thermistor probes in the chromatograph column produce a linear electrical response proportional to sample concentration at least for sample sizes used in these experiments.

4. A binary sample of pentane and heptane will not separate on the 100 cm chromosorb 102 column given the limitations of the test facility.

5. Data from the DES column show that samples run on this column are well modeled by the equilibrium adsorption model. Separation of the pentane - heptane binary mixture is well represented by the linear superposition of pure component data.

6. Data for heptane on C-102 over a range of sample sizes have shown that the variation of mR_o with composition is a non-interactive effect. A nonlinear Langmuir isotherm is expected to bring the model closer to actual data.

7. Solution of the model with a Langmuir isotherm using orthogonal collocation has shown qualitatively that this model

can predict the composition dependent mR_0 and the tailing found for samples on C-102.

It is recommended that the Langmuir isotherm model be studied more closely to find out what values of K would be applicable to the experimental system. A method for solving the model more accurately should be sought. The method of orthogonal collocation is extremely flexible and might be modified to better suit this problem. Other numerical techniques might also be studied.

VI. ACKNOWLEDGEMENT

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VII. NOMENCLATURE

E_a - Activation energy of adsorption

K - Langmuir isotherm constant ($= 1/m$)

mRo - Thermodynamic Parameter

Pe - Peclet number

R - Gas constant

T - Temperature

x - Fraction of filled adsorption sites

y - Sample concentration in the gas stream

z - Dimensionless distance along the length of the column

θ - Dimensionless time (vt/L)

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IX. APPENDICES

A. Data Processing Modifications

- 1) listing of GDRP with STATMO
- 2) listing of binary analysis program
- 3) listing of binary simulation program MODEL
- 4) listing of SIM

B. Calculation of Mole Fractions

C. Data Showing Thermistor Linearity

D. Calculation of Activation Energy of Adsorption

E. Derivation of Langmuir Isotherm Model

F. Details of Orthogonal Collocation Solution

G. Listing of Langmuir Isotherm Model Program

H. Listing and Data of Eigenanalysis Program

The appendices were not included in the report because of their length. Copies may be obtained upon request from:

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